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THIRD EDITION

Properties of Matter

by

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PREFACE

The subjects comprising the Properties of Matter form an ill-defined group and the authors have attempted to treat selected topics adequately rather than to cover a very wide field. It is felt that the advanced student, for whom this book is primarily intended, will already be familiar with the simple physical principles underlying Kinematics, Dynamics, Central Orbits and Gyroscopic Motion. These subjects have therefore been omitted, for their advanced study can be profitably pursued only from the mathematical standpoint. The aim throughout the present work has been to treat the matters considered from a physical point of view, and particularly to avoid regarding the material as exercises in applied mathematics. For example, the propagation of longitudinal and transverse waves is immediately associated here with the geophysical problems of Seismic Waves.

The introduction of newer and more accurate methods for measuring various quantities such as the Newtonian Constant of Gravitation has necessitated only brief reference to older methods, but classical work such as that of Boys has been fully described.

It is now impossible to draw a dividing line between General Physics and Physical Chemistry in some topics. A concise account of Debye and Hückel's theory of strong electrolytes has therefore been given, and a whole chapter has been devoted to the new and important subject of Surface Films.

The authors have tried as far as possible to indicate the original sources of their material by references in the text and at the end of the chapters. They take this opportunity of apologizing to any writer whose work may inadvertently have been used without acknowledgment.

F. C. CHAMPION.

N. DAVY.

PREFACE TO THE SECOND EDITION

The main framework of the original book remains unaltered, but it is inevitable that after a period of fifteen years some changes should have proved necessary. These changes sometimes take the form of (1) the insertion of more accurate values of the fundamental constants, (2) the replacement of older experimental methods by newer methods which are superior because of improvements in technique, and (3) the addition of recently acquired knowledge. The first change occurs in the values of the fundamental constants used in the chapter on Errors of Measurement. Examples of the second change are the recent accurate measurement of g , the acceleration due to gravity, and the introduction of the microdiffusiometer by Furth and Zuber, for the rapid and accurate measurement of diffusion coefficients of solutions. Fresh knowledge has been collected in the form of modern views on the nature of the angle of contact in capillarity, on the diffusion processes in gases, and on the viscous properties of non-Newtonian fluids. Finally a few additional examples and hints for solution have been added to illustrate the use of the new material.

F. C. CHAMPION
N. DAVY.

LONDON AND NOTTINGHAM
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PREFACE TO THE THIRD EDITION

The ever-increasing rate of advance of knowledge has necessitated the production of a third edition, following the second edition after a period of time which is only half that which elapsed between the first and second editions. As before, the main framework of the book remains unaltered but the relative importance of the various topics has changed. For example, the apparent simplicity of capillarity, which may be static, compared with diffusion which must be dynamic, has proved to be deceptive, for a study of diffusion is giving greater insight into the nature of the liquid state. A few sections have therefore been deleted from the chapter on capillarity although a section has been added on paper chromatography which depends on simultaneous diffusion and capillary action.

In the earlier editions, atomic and molecular concepts were largely confined to the chapter on the kinetic theory of matter but the power and range of these concepts have now invaded other chapters. Thus in Chapter I, the unit of time may be defined primarily from an atomic clock, while in Chapter IV a new section has been added on the elasticity of single cubic crystals where the behaviour is found to depend on the nature of the forces between the atoms on the cubic lattice. In Chapter IX, diffusion in solids is interpreted in terms of vacant atomic sites and interstitial atoms and in Chapter XII these ideas are extended to explain viscosity and diffusion in liquids. Finally in Chapter XIII, a new section has been added on the present values of the atomic constants. However, the important change in the present edition is not primarily the deletion or the addition of particular topics but the gradual orientation of the subject from a largely phenomenological treatment to atomic interpretations.

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N. DAVY.

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PROPERTIES OF MATTER

CHAPTER I

Units and Dimensions

1. Introduction.

The statement that a given body weighs 10 pounds implies that a given unit of weight, the pound, has been chosen, and that the ratio of the weight of the body to that of the unit is 10. In general, a *conventional* choice of certain units is made, and any physical entity may then be expressed by a number which states how many of these units the entity in question contains. The units chosen should be (1) well defined, (2) not subject to secular change, (3) easily compared with similar units, (4) easily reproduced.

Physical laws consist in the relations which have been found to exist between the numbers which represent physical quantities. Hence although each type of physical quantity requires its own unit, these units are not necessarily independent; actually, many of the units may be expressed in terms of a certain few, called *fundamental units*. The choice of the latter is initially quite *arbitrary*, but when once settled it is fundamental for subsequent work. Gauss called such a system of units an *absolute system*, but the term is unfortunate, since the system chosen is quite conventional. There are, in fact, several "absolute" systems of units in use, depending on the fundamental units chosen and the physical laws used in expressing the remaining *derived units*. Thus there is the *British system* with the *foot*, *pound*, and *second* as the fundamental units, while that used for purely scientific work is almost invariably the C.G.S. or centimetre, gramme, and second system.

2. Fundamental Units.

Three of the fundamental units which have been chosen are those of *mass*, *length*, and *time*, and many physical units may be expressed in terms of these three. If, however, physical entities other than those

which have an immediate "explanation" in "mechanical" terms are under consideration, additional fundamental units are required. For example, in the science of heat the *calorie* is the fundamental unit of quantity of heat in the C.G.S. system, again, the *unit degree Kelvin* is adopted as the fundamental unit of temperature in the same system.

The British unit of mass is the *pound avoirdupois*, which is simply the mass of a piece of platinum preserved in the Standards Department of the Board of Trade and marked "P.S. 1844, 1 lb". It bears no simple relation to the unit of volume in the same system and thus differs from the unit of mass in the French or metric system. This, the *kilogramme*, was initially made as close as possible to the weight of 1000 c.c. of water at its temperature of maximum density. Although subsequent work has shown that this relation is not quite accurate, the original kilogramme has been retained and is now simply taken as the weight of a mass of platinum preserved at the International Bureau of

Weights and Measures, Paris, is quite arbitrary in the British system, the yard being defined as the straight distance between the transverse lines in two gold plugs on the bronze bar at 62° F (°) preserved in the Standards Department of the Board of Trade. In the

metric system, the *metre* is now simply taken as the distance between two marks on the platinum bar at 0° C preserved at the International Bureau of Weights and Measures, near Paris.

Both systems have the same unit of time, the *mean solar second*, which is simply the mean solar day divided by 86,400. Recently there has been some discussion as to whether the units of length and time as defined above are sufficiently independent of secular change. For example, the metal bars taken as the standards of length are under-

going to be replaced by optical standards. It has been evolved more constant units of length and time, expressed in terms of more fundamental quantities such as the wavelength of an optical line emitted from an atom and the reciprocal of the frequency of a specified optical emission from another atom, respectively. Variations in the mean solar second have certainly been demonstrated by both the optical standard and by use of a quartz oscillator.

3. Derived Units.

Consider now the expression for the area of a surface. The unit in which the area is expressed is the area of a square whose side is

the unit of length. Similarly, the unit in which a volume is expressed is that of a cube whose side is the unit of length. Further, the unit in which a velocity is expressed is obtained by dividing the unit of length by the unit of time. Such units, which depend on powers of one or more of the fundamental units, are termed derived units. The unit of area is often represented symbolically by L^2 , that of volume by L^3 , and that of velocity by $V = L/T$ or LT^{-1} , and these expressions are called the *dimensional formulae* of the quantities considered. Again, the dimensions of a physical quantity may be defined as the powers of the fundamental units in terms of which it may be expressed. Area and volume, therefore, have dimensions two and three in length respectively.

The dimensional formula for mechanical energy is $E = MV^2 = ML^2T^{-2}$. Since (in Newtonian mechanics, at least) the numerical measure of energy is *one-half* the product of the number representing the mass and the square of the number representing the velocity, dimensional formulae are neither complete numerical laws nor even definitions. The dimensional formula merely states (1) the nature of the experiments (i.e. of length, mass, &c.) on the fundamental quantities which must be made in order to determine the given quantity, (2) the powers to which the primary quantities have to be raised. It is clear that (2) will be important in deciding on the accuracy of measurement required in any part of an experiment.

4. Dimensional Analysis.*

The study of dimensional analysis will be introduced by the consideration of a simple example. The elementary formula for the time of

*The best method of presenting dimensional analysis and its relation to the principle of dynamical similarity is still a subject of acute discussion, but the writer (E. C. U.) has attempted to present a set of rules which are consistent and which do not lead to error in any applications so far considered. It should be mentioned that controversy also exists concerning the rival merits of various systems of units since it is possible to define systems in which dimensional constants such as the gravitational constant and the velocity of light are unity; such systems are said to be *rational*. While such schemes may simplify the algebra of a given analysis, they often make it impossible to apply checks by dimensional analysis. Moreover, they impose an arbitrary selection and rearrangement of the concepts evolved in the historical development of the subject as when the concept of the single magnetic pole is discarded and replaced entirely by the magnetic field associated with circuit elements of electric current. Undoubtedly a time sometimes comes when over-adherence to the historical method may become more confusing than enlightening, as for example would apply to any modern detailed discussion of oxidation, on phlogiston theory or of simultaneous reflection and refraction of light at an interface on Newton's theory of the "fits" of optical corpuscles. Nevertheless, science abounds in convenient *fruitful* fictions as varied as the concepts of surface tension, the billiard-ball atom and the various models of the atomic nucleus now extant, such as the liquid-drop model, the independent particle model and the cloudy crystal ball model. It is therefore simply pointed out here that while alternative systems of units and of dimensions are possible, no overwhelming case has yet been made out for the general adoption for all purposes of such units as those of the rationalized systems or of the M.K.S. (metre-kilogram-second) system, in preference to those already defined in § 2.

oscillation of a simple pendulum in the earth's gravitational field is

$$t = 2\pi \left(\frac{l}{g} \right)^{\frac{1}{2}}, \quad \dots \dots \dots (1)$$

where l is the length of the pendulum and g is the acceleration due to gravity. As this is purely a mechanical problem, the variables t , l and g may all be expressed in terms of the three primary quantities, M , L and T . Writing down the dimensional formulae, we have

$$t = T, \quad l = L \quad \text{and} \quad g = LT^{-2}.$$

The 2π is a so-called pure number; since it does not depend on a fundamental physical unit, it cannot be represented in dimensional analysis. It is interesting to note that π may be obtained experimentally as the ratio of the circumference of a circle to its diameter, and since both are measured in the same units, the units are eliminated. Now the L.H.S. of equation (1) clearly has the dimensions T , while the R.H.S. has dimensions

$$(L/LT^{-2})^{\frac{1}{2}} = T,$$

Hence the dimensions of both sides of the equation are the same. The property is true of all equations representing possible physical phenomena, and may be stated as follows:

✓ Law I.—*Physical equations must be dimensionally homogeneous.*

Should any equation contain more than a single term, that is $t = f(A) + f(B) + \dots$, then each individual term $f(A)$, $f(B)$, must be of the dimensions of time only. Alternatively, an expression may not be a simple power function but may consist of more complex functions. For example, the equation for a simple harmonic displacement x is $x = a \sin pt$, where a is the amplitude and p the angular frequency. This is obviously dimensionally homogeneous since x and a have the same dimensions while $pt = \theta$, where θ is an angle and is therefore dimensionless. Similarly, if the expression is exponential it is often of the

when

time

T^{-1}

then

initial value, and is termed the *time of relaxation*.

Consider now the inverse problem. Suppose that the equation for the time of oscillation of a simple pendulum is not known. From the physical nature of the problem the time of oscillation might reasonably be expected to depend upon the following quantities. l , the length of the pendulum, m , the mass of the bob, and g , the acceleration due to gravity. Then

$$t = f(m, l, g), \quad \dots \dots \dots (2)$$

where the nature of the function f has to be found. Assume that the R.H.S. of (2) may be expressed as a *power formula*. Then

$$t = km^{-\alpha}g^{\gamma}, \quad \dots \dots \dots (3)$$

where k is a possible dimensionless constant which will not be represented in the dimensional analysis. Writing (3) in its dimensional form, we have

$$T = M^{\alpha}L^{\beta}LT^{-2\gamma}. \quad \dots \dots \dots (4)$$

The indices of the primary quantities on the two sides of (4) must be equal if Law I is true. Hence

- | | |
|-------------|-----------------------|
| (1) length: | $0 = \beta + \gamma,$ |
| (2) mass: | $0 = \alpha,$ |
| (3) time: | $1 = -2\gamma.$ |

Substituting in (3), we have

$$t = k\left(\frac{l}{g}\right)^{\frac{1}{2}}. \quad \dots \dots \dots (5)$$

5. Dynamical Similarity.

Consideration of equation (5) shows that the problem may be regarded in another way, namely, as involving not three variables t , l and g , but a single variable $t(g/l)^{\frac{1}{2}}$, which groups together a whole system of experiments of essentially the same type. In the foregoing analysis the time t might have been taken to represent the time required for the pendulum to swing out to a given angle α ; then $t = k\sqrt{l/g}$, where k is now constant only when α is constant. If at different places where the accelerations due to gravity are g_1 and g_2 , pendulums of lengths l_1 and l_2 are allowed to oscillate, then both pendulums will pass through the same angular displacement at times t_1 and t_2 given by $t_1(g_1/l_1)^{\frac{1}{2}} = t_2(g_2/l_2)^{\frac{1}{2}}$. Systems which can be grouped together quite generally as passing through identical phases for equal values of a dimensionless grouping of corresponding quantities are said to possess dynamical similarity. Simple geometrical similarity, however, is not necessarily a sufficient condition for dynamical similarity. For example, two compound pendulums would not be dynamically similar if the density of the material of which they were composed were not distributed in both in identically the same way.

6. Uses and Limitations of Dimensional Analysis.

Dimensional analysis affords a simple and rapid solution of physical problems, but this advantage is offset by the lack of information on the presence of pure numbers. It is true that the latter can be determined by experiment, subsequent to the analysis, but matters are

further complicated by the presence of *dimensional constants* like G , the gravitational constant. As an example of this difficulty, suppose it is required to find the time of revolution of one body revolving round another under mutual gravitational forces. Then

$$t = f(m_1, m_2, r), \quad \dots \quad (6)$$

where r is the distance between the two bodies and m_1, m_2 are their masses. Now since the L.H.S. of (6) has the dimensions of T and the R.H.S. dimensions only of M and L , there appears to be no solution. Physical judgment suggests that a relevant variable may have been omitted from the R.H.S. of (6), and the gravitational constant G is introduced. If force is already considered to be defined by Newton's second law of motion, G is a dimensional constant given by Newton's law of gravitational attraction, $F = G \frac{m_1 m_2}{r^2}$ or $G = M^{-1} L^3 T^{-2}$. Hence (6) becomes

$$t = f(m_1, m_2, r, G) = k m_1^a m_2^b r^c G^d. \quad \dots \quad (7)$$

Writing down the dimensional formulae and equating the indices of the same primary quantities, we have

$$\left. \begin{array}{ll} (1) T & 1 = -2\delta, \\ (2) M & 0 = \alpha + \beta - \delta, \\ (3) L & 0 = \gamma + 3\delta. \end{array} \right\}$$

Since there are four unknowns and only three equations, the final solution of (7) may be written in terms of one of the unknowns:

$$t = k m_1^{(-1-\delta)} m_2^{\delta} G^{-\delta} r^{\delta} = k \frac{r^{\delta}}{G^{\delta} m_1^{\delta}} \left(\frac{m_2}{m_1} \right)^{\delta}. \quad \dots \quad (8)$$

Now $(m_2/m_1)^{\delta}$ is dimensionless and therefore its value cannot affect the dimensional homogeneity of (8). It may therefore be present as a function of any type and (8) may be written in the general form

$$t = k_1 \frac{r^{\delta}}{G^{\delta} m_1^{\delta}} f\left(\frac{m_2}{m_1}\right) \quad \dots \quad (9)$$

The preceding problem involved one unknown function, and, in general, the number of unknowns that ultimately remain is equal to the difference between the number of variables and the number of primary quantities considered. In *dimensional analysis*, therefore, three main questions arise.

- (1) What dimensional constants are to be introduced?
- (2) How many variables are to be used, and which?
- (3) How many primary quantities are to be considered?

It may be stated at once that the answering of these questions is a matter for physical intuition; that is, physical intuition, acting over long experience, decides from known solutions of problems analogous to the one requiring solution that certain variables are likely to be relevant and others irrelevant.

The main uses of dimensional analysis are as follows:

(1) *To test the correctness of equations.*

After a long analysis it is useful to check the final equation for dimensional homogeneity by substitution of the dimensional formulae on both sides of the equation.

(2) *To derive equations without complete analysis.*

If the differential equation appropriate to any physical problem can be formulated and solved, a complete solution of the problem is possible. The solution contains, in general, the same number of physical variables and dimensional constants as the original differential equation. When the problem is complicated, the formulation of the differential equation is often impossible. Recourse is then made to dimensional methods, and if the relevant variables and dimensional constants can be guessed correctly, at least a partial analysis is possible. Frequently the intermediate case occurs: the differential equation can be formulated but not solved; the variables to be used in the dimensional analysis are then known.

(3) *To recapitulate important formulae.*

With a complicated formula, such as Poiseuille's equation for the flow of a viscous liquid through a right circular cylinder, it may be easier to recover the equation from a knowledge of the dimensions of viscosity than to memorize it or deduce it from first principles.

(4) *To suggest relations between fundamental constants.*

This is a dubious use of dimensional analysis and will only be briefly considered. The existence of dimensionless grouping is often found to indicate a relation between the components of the group. If we consider the fundamental constants

$$\left\{ \begin{array}{l} G, \text{ the gravitational constant,} \\ e, \text{ the charge on the electron,} \\ m, \text{ the mass of the electron,} \\ c, \text{ the velocity of light,} \\ h, \text{ Planck's constant of action,} \end{array} \right.$$

we find that (hc/e^2) is dimensionless, and $(hc/2\pi m c^2)$ is actually a factor which is constantly involved in the wave mechanical and quantum treatment of the interaction of atomic particles. Again, G has the

same dimensions as $(e/m)^2$, and this may indicate an electromagnetic theory of gravity. The relation is not, however, likely to be simple, since the ratio $(e/m/e)^2$ is about 10^{-42} . In the preceding example $(hc/2\pi e^2)$ is equal to 137.

7. Extension of Dimensional Analysis.

Consider now the dimensional formula for κ , the coefficient of thermal conduction. The constant κ is defined by the differential equation

$$\frac{dQ}{dt} = \kappa A \frac{d\theta}{dx}$$

where A is the area of each of two planes situated a distance dx apart and maintained at a difference of temperature $d\theta$; dQ is the amount of heat flowing across in time dt . If Q , θ , M , L and T are taken as primary quantities, the dimensional formula for κ is $Q\theta^{-1}L^{-1}T^{-1}$. Inspection of this formula shows that for geometrically similar bodies of uniform conductivity and similar temperature distributions, the quantity of heat transferred across corresponding cross-sections is proportional to the time, the conductivity, the linear dimensions, and the maximum temperature difference.

This conclusion, however, does not follow if the number of primary quantities is reduced. For example, Q is often assigned the dimensions of mechanical energy ML^2T^{-2} , from Joule's law $Q = E/J$, where Q is the quantity of heat which appears when a certain amount of mechanical energy E disappears. Similarly θ is often given the same dimensions, ML^2T^{-2} , from the equation of a perfect gas, $pV = R\theta$. The crucial point is whether J and R are dimensional or dimensionless constants. Now the problem of heat conduction is concerned neither with the "equivalence" of heat and mechanical energy, nor with the properties of perfect gases. It is therefore illegitimate to assign the dimensions of energy to either Q or θ in the case of heat conduction.

Consider, however, the dimensional formula for entropy. The concept of entropy was initially deduced from considerations of (1) the properties of gases, (2) the relation between heat and mechanical energy. In this case, therefore, both Q and θ may be given the dimensions of mechanical energy. Since the change of entropy is given by dQ/θ , entropy is seen to be dimensionless. If, on the other hand, quantity of heat were defined by the expression $Ms\theta$, where s is the specific heat (itself a ratio, since it may be defined as the ratio of the amount of heat required to raise a given mass of the material through a given temperature range, to that required to raise the same mass of a standard material (water) through the same temperature range), the dimensions of entropy would clearly be those of mass. Now the entropy of the universe is continually increasing; it is much more

probable that some purely dimensionless quantity rather than the total mass is undergoing this change. Further, the dimensionless formula is in agreement with statistical theory.* The above results may be summed up in Law II:

Laws that are not directly relevant to the problem under consideration must not be used to assign dimensions.

The implications of Law II must be strictly followed out in assigning dimensions to κ , the dielectric constant, and μ , the magnetic permeability. If the problem is directly associated with Coulomb's law $F = q_1 q_2 / \kappa r^2$, where F is the force between two point charges q_1 and q_2 separated by a distance r in an enveloping medium of dielectric constant κ , electrostatic dimensions are appropriate. If the problem is directly connected with Ampère's law, electromagnetic dimensions must be assigned. In the special case where κ is the same for all the components involved in the problem, κ may be regarded as being dimensionless, since it may be defined as the ratio of the capacities of two identical condensers, one of which is filled with the dielectric and the other empty. Similarly, if the problem is entirely electromagnetic and μ is constant, the latter may be regarded as dimensionless.

8. Examples of Dimensional Analysis.

The preceding principles will now be illustrated by examples from different branches of physics; further examples for the reader will be found at the end of the book.

(1) Mechanics. *Motion of a body through a resisting medium.*

Suppose it is required to find how the resistance to bodies of similar shape but different size depends on the variables of the problem. Guessing the variables and writing down their dimensional formulae, we have

(a) Resisting force	R	MLT^{-2} ,
(b) Velocity	v	LT^{-1} ,
(c) Linear dimensions	d	L ,
(d) Density of resisting medium	ρ	ML^{-3} ,
(e) Viscosity of resisting medium	η	$ML^{-1}T^{-1}$.

Let

$$R = kv^\beta d^\gamma \eta^\delta;$$

then we have

$$MLT^{-2} = L^\alpha T^{-\alpha} M^\beta L^{-3\beta} L^\gamma M^\delta L^{-\delta} T^{-\delta},$$

hence

$$\begin{aligned} (1) \quad M & 1 = \beta + \delta, \\ (2) \quad L & 1 = \alpha - 3\beta + \gamma - \delta, \\ (3) \quad T & -2 = -\alpha - \delta. \end{aligned}$$

* In *The Nature of the Physical World* (Cambridge University Press, 1929), Eddington defines increase of entropy as "the increase of the random element in the universe . . . a measure of the continuous loss of organization of the universe". This agrees with the dimensionless formula.

Let α remain uneliminated, then

$$R = k \left(\frac{v \rho d}{\eta} \right)^2 \frac{\eta^3}{\rho}$$

$$R = k \frac{\eta^3}{\rho} f \left(\frac{v \rho d}{\eta} \right). \quad \dots \dots \dots (10)$$

Now systems for which the dimensionless expression $(v \rho d / \eta)$ is constant possess dynamical similarity. For bodies of similar shape with η and ρ constant, the resisting force R is therefore the same if vd is constant. Hence the law of similar speeds, that for the same resistance to motion the velocity is inversely proportional to the linear dimensions, has been deduced. It is therefore advantageous to construct large airships rather than small ones, since the lifting power is approximately proportional to the volume, that is, depends on L^3 . With very fast aeroplanes, the velocity of sound must be included as a further variable.

(2) Heat Convection.

Attention will here be confined to natural convection, the problem of forced convection being treated in Chapter XII. The variables which enter into the problem are:

- | | | |
|---------------------------------------|----------|---------------------------------|
| (a) Temperature of the body | θ | θ . |
| (b) Linear dimensions of the body | l | L . |
| (c) Thermal conductivity of the fluid | κ | $Q \theta^{-1} L^{-1} T^{-1}$. |

will certainly be required. To avoid having to consider the density of the fluid, we use the remaining variables in the following form

- | | | |
|--|----------|--------------------------|
| (d) Thermal capacity of the fluid per unit volume | c | $Q \theta^{-2} L^{-3}$. |
| (e) Acceleration of gravity | g | $L T^{-2}$. |
| (f) Temperature coefficient of density change of the fluid | α | θ^{-1} . |
| (g) Kinematic viscosity | ν | $L^2 T^{-1}$. |

The quantities (e) and (f) are grouped together in the form of the product ga . This is justified by the fact that the upward thrust on unit volume of the fluid of density $\rho - \Delta \rho$, if the surrounding fluid has density ρ , is $g \Delta \rho$, and since the mass of the fluid is ρ , the acceleration produced on the fluid will be proportional to $g \Delta \rho / \rho$, which in turn is proportional to $g \frac{1}{\rho} \frac{d\rho}{d\theta}$ or ga , where a is the temperature coefficient of density change of the fluid. The effect of change of density on the viscosity of the fluid is thereby neglected, in practice, the viscosity is taken to be that of the fluid at a temperature which is the mean of that of the body and the main bulk of the fluid. Finally, the viscosity is used in the form of the kinematic viscosity $\nu = \eta / \rho$, where η is the ordinary coefficient of viscosity defined in Chapter XII (p. 271).

Writing the required relation as a power formula in the usual way, we have

$$h = \theta^a \kappa^b c^\gamma (ga)^{\delta} \nu^\epsilon$$

or

$$Q L^{-2} T^{-1} = \theta^a Q^b L^{-2} \theta^{-2b} T^{-b} T^{-\gamma} L^{-3\gamma} L^{2\gamma} \theta^{-2\gamma} Q^{-\delta} L^{\delta} L^{2\delta} T^{-\delta}$$

- | | |
|--------------|---|
| (1) Q | $1 = b + \gamma - \delta$. |
| (2) L | $-2 = -b + \delta + \epsilon + 2\delta - 3\gamma$. |
| (3) T | $-1 = -b - \mu - 2\delta$. |
| (4) θ | $0 = a - b - \gamma - \delta$. |

Expressing the other unknowns in terms of δ and μ , we have

$$\begin{aligned}\alpha &= 1 + \delta, \\ \beta &= 1 - 2\delta - \mu, \\ \gamma &= 2\delta + \mu, \\ \epsilon &= 3\delta - 1.\end{aligned}$$

Substituting these values in the expression for h , we obtain three interrelated dimensionless groups:

$$\frac{h}{\theta x} = \left(\frac{\partial g a c^2 d^2}{x^2} \right)^{\delta} \left(\frac{c v}{x} \right)^{\mu},$$

or in general,

$$\frac{h}{\theta x} = F \left(\frac{\partial g a c^2 d^2}{x^2} \right) f \left(\frac{c v}{x} \right). \quad \dots \dots \dots (11)$$

Consider the application of these formulae to cylinders whose length is great compared with the diameter. Then h depends only on the diameter d , and d may be substituted for l . Further, if H is the heat lost per unit length per second per degree temperature excess, we have

$$H = \frac{\pi h d}{6};$$

hence

$$\frac{H}{x} = F \left(\frac{\partial g a c^2 d^2}{x^2} \right) f \left(\frac{c v}{x} \right). \quad \dots \dots \dots (12)$$

For cylinders surrounded by diatomic gases, (1) $c v/x$ is nearly constant; (2) $1/v^2$ may be written for c^2/x^2 in the first function, since the two expressions have the same dimensions; (3) g is constant, and for a constant temperature of the surrounding gas, a is the same for all gases; hence we have

$$\frac{H}{x} = F_1 \left(\frac{\theta d^2}{v^2} \right). \quad \dots \dots \dots (13)$$

Plotting the values of H/x as ordinates and the corresponding values of $\theta d^2/v^2$ as abscissæ, we find that for the natural convective cooling of long cylinders all the points lie on a single curve.* The agreement between the results for steam-pipes and those for fine wires is very remarkable.

(3) Light. *The blue of the sky.*

The law governing the scattering of light by small obstacles was first deduced dimensionally by the late Lord Rayleigh. The variables which present themselves are:

(a) Amplitude of the incident wave	a	L ,
(b) Volume of obstacles	v	L^3 ,
(c) Distance of point considered from obstacle	r	L ,
(d) Wave-length of incident light	λ	L .

Then the amplitude of the scattered wave at r is

$$s = k \frac{a v \lambda^{\alpha}}{r^{\beta}}, \quad \dots \dots \dots (14)$$

since s is known to be proportional to a and v and inversely proportional to r . To make the equation dimensionally homogeneous, we must have $\alpha = -2$. Since the scattered intensity is proportional to the square of the scattered amplitude, the amount of light scattered is inversely proportional to the fourth power

* Cf. Roberts, *Heat and Thermodynamics*, p. 297 (Bischofs & Son, Ltd., fourth edition, 1951).

of the wave length. This is almost sixteen times as great for the violet as for the red end of the spectrum. Consequently the blue present in white light is scattered to a much greater extent than the red.

(4) Sound. *Tuning-forks of similar shape.*

For tuning-forks of similar shape and of isotropic material, the restoring force is due to the elasticity of the prongs, and the time of oscillation t will depend on the following quantities.

(a) Linear dimensions of the fork	l	$L,$
(b) Young's modulus of the material	q	$ML^{-1}T^{-2},$
(c) Density of the material	ρ	$ML^{-3},$

Hence

$$t = Klq^a \rho^r,$$

or, dimensionally,

$$T = L^\alpha M^\beta T^{-2\beta} L^{-3\gamma} M^\gamma L^{-3\gamma},$$

We have

$$\begin{aligned} (1) \quad M & 0 = \beta + \gamma, \\ (2) \quad T & -2 = -2\beta, \\ (3) \quad L & 0 = \alpha - \beta - 3\gamma. \end{aligned}$$

Hence

$$t = klq^{-1}\rho^{\frac{1}{2}}. \quad \dots \dots \dots (15)$$

(5) Electricity and magnetism. *Electromagnetic mass of a charged sphere*

The most likely variables would seem to be these:

(a) Charge	q	$M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-1},$
(b) Radius of sphere	a	$L,$

Hence

$$m = kq^2 a^3.$$

This equation is dimensionally inhomogeneous in T ; as a further variable we try the constant c , which is the ratio of the units of charge in the electromagnetic and electrostatic systems respectively. Its dimensions are those of a velocity; hence

$$m = kq^2 a^3 c^2.$$

or, dimensionally,

$$M = M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-1}T^{-2}L^3L^3T^{-2}.$$

We have

$$\begin{aligned} (1) \quad M & \frac{1}{2} = 1, \\ (2) \quad L & 0 = \frac{3}{2} + \beta + \gamma, \\ (3) \quad T & 0 = -\alpha - \gamma, \end{aligned}$$

or

$$m = \frac{kq^2}{ac^2} \quad \dots \quad (16)$$

Complete analysis gives $k = 2/3$.

REFERENCES

1. *THEORY OF UNITS AND DIMENSIONS*

2.

3. *THEORY OF UNITS AND DIMENSIONS*

4.

CHAPTER II

The Acceleration Due to Gravity

1. Introduction.

The force on a body situated at a point in the gravitational field of the earth can be written in the form mg , where m is the mass of the body and g is a quantity known as the acceleration of gravity, or the acceleration of a body falling freely in vacuo, at that point. It is also the strength of the gravitational field at the point, for it is the force on unit mass. Owing to the spin of the earth, the direction and magnitude of the vector g will depend on the latitude (see Ex. 1, Ch. II, p. 311). The quantity g is independent of the mass of the body concerned. The most accurate methods of measuring g now in use are based upon pendulum observations. It is convenient to summarize the development of the theory and practice of this work.

2. Simple Pendulum with Friction.

We take it for granted that the student knows how to obtain the expression $T_0 = 2\pi(l/g)^{1/2}$ for the period of a simple pendulum. The assumptions involved are that the pendulum consists of a particle suspended from a rigid support by an inelastic string of negligible mass, and that it oscillates in vacuo with oscillations of infinitely small amplitude. When the viscous drag of the medium on the bob is not neglected, the equation of motion is altered. Let θ be the angular displacement (fig. 1). Experiment proves that the viscous retarding force is proportional to the linear velocity of the bob $l\dot{\theta}$ and to the viscosity of the medium. The moment of this force about an axis through the point O , perpendicular to the plane of the figure, may be written in the form $k\dot{\theta}$, where k is a constant and l is the length of the string. The weight gives rise to a restoring moment $mg l \sin \theta$, which when θ is small may be taken as $mg l \theta$. Hence the equation of rotational motion about the axis through O is

$$ml^2\ddot{\theta} + k\dot{\theta} + mgl\theta = 0, \quad \dots \quad (1)$$

for $ml^2\ddot{\theta}$ is the product of the moment of inertia and the angular acceleration.

If we divide throughout by ml^2 and write $k/ml = 2b$ and $g/l = c^2$, the equation becomes

$$\ddot{\theta} + 2b\dot{\theta} + c^2\theta = 0. \quad \dots \quad (2)$$

The general solution of this equation may be written in the form

$$\theta = Ae^{-bt} \cos\{(c^2 - b^2)^{1/2}t + \phi\}. \quad \dots \quad (3)$$

It represents what are called *damped* (that is, decaying) *oscillations*, whose period is given by

$$T = 2\pi/(c^2 - b^2)^{1/2} = 2\pi/(g/l - b^2)^{1/2}. \quad \dots \quad (4)$$

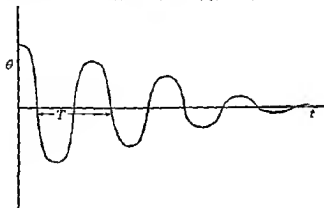


Fig. 2

A graph connecting θ and t reveals the decay of the oscillations. In fig. 2, ϕ is assumed to be equal to zero. On comparing $T = 2\pi/(g/l - b^2)^{1/2}$ with the simple formula $T_0 = 2\pi/(g/l)^{1/2}$, we see that $T/T_0 = \{g/l/(g/l - b^2)\}^{1/2} = \{1 - b^2/g\}^{-1/2}$. In the practical case of a pendulum vibrating in air b is small, and the expression on the right may be expanded to two terms by the binomial theorem, giving $T/T_0 = 1 + b^2/2g$ approximately. Writing $T_0 = 2\pi(l/g)^{1/2}$ and $l/g = T_0^2/4\pi^2$, we have

$$T/T_0 = 1 + b^2T_0^2/8\pi^2. \quad \dots \quad (5)$$

For a pendulum in air, this slightly exceeds unity, the second term representing the correction for viscous drag of the air on the bob.

3. Pendulum with Finite Amplitude of Swing.

If θ is so large that it is not permissible to write $\sin \theta = \theta$, equation (1) must be replaced by

$$m l^2 \ddot{\theta} + k l \dot{\theta} + m g l \sin \theta = 0. \quad \dots (6)$$

For the present purpose, which is simply to find the effect of a finite amplitude of swing, the viscous term $k l \dot{\theta}$ may be neglected, giving

$$m l^2 \ddot{\theta} + m g l \sin \theta = 0. \quad \dots (7)$$

The solution of this equation is beyond the scope of the present book. The period of oscillation is found to be

$$T = 2\pi K(\theta) (l/g)^{1/2}, \quad \dots (8)$$

where $K(\theta)$ is a function of θ , known as a *complete elliptic integral of the first kind*. It can be expanded in a series of sines of $\theta/2$, giving

$$T = 2\pi (l/g)^{1/2} \{1 + (1/2)^2 \sin^2 \theta/2 + (1/3 \cdot 2 \cdot 4)^2 \sin^4 \theta/2 + \dots\}.$$

When θ is fairly small, we may replace $\sin \theta/2$ by $\theta/2$ in the second term and neglect subsequent terms; then

$$T = 2\pi (l/g)^{1/2} \{1 + \theta^2/16\} = T_0 \{1 + \theta^2/16\}. \quad \dots (9)$$

4. Pendulum with a Large Bob.

Consider the small oscillations of a pendulum composed of a heavy spherical bob of mass M and radius R cm., on an inextensible string of negligible mass (fig. 3). Assume that the bob moves so that the same radius PQ constantly lies along the straight line PO joining the centre of the bob P to O , the point of support; that is, that the bob is simply oscillating about an axis through O , perpendicular to the plane of the figure. The moment of inertia of a sphere about an axis parallel to a diameter, and l cm. from it, is $2MR^2/5 + Ml^2$, by the theorem of parallel axes. The equation of rotational motion for small oscillations (viscous forces being neglected) is

$$(2MR^2/5 + Ml^2) \ddot{\theta} + Mgl\theta = 0. \quad \dots (10)$$

Hence the period of oscillation is

$$T_1 = 2\pi \{(2R^2/5 + l^2)/lg\}^{1/2}. \quad \dots (11)$$

A real pendulum would scarcely swing in the assumed manner; its bob would oscillate about Q after the string had reached its extreme position on either side. The supporting fibre would have a definite mass and moment of inertia. These and other defects cause the rejection of this apparatus as a means of measuring g accurately.

5. Compound Pendulum.

Accurate methods of measuring g are chiefly based on the measurement of the period of small oscillations of a compound pendulum, that is, of a rigid body, about a fixed horizontal axis, which is usually a metal knife-edge. Fig. 4 represents a rigid body, suspended so as to be perpendicular to the plane of gravity when in a displaced position about an axis through O is Mk^2 , that about a parallel axis through O is $Mk^2 + MI^2$, by the

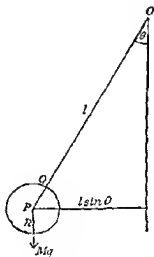


FIG. 3

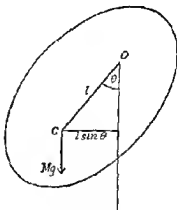


FIG. 4

theorem of parallel axes. The equation of rotational motion about the axis through O , if we neglect viscous forces and write θ for $\sin \theta$, is

$$(Mk^2 + MI^2)\ddot{\theta} + Mgl\theta = 0, \quad \dots (12)$$

giving a period

$$T = 2\pi\{(k^2 + l^2)/gl\}^{1/2}. \quad \dots (13)$$

A graph connecting T and l has the form shown in fig. 5. To obtain such a graph experimentally, a metal bar with numerous holes drilled in it is swung from a fixed peg through any one of the holes. The centre of gravity of the bar can be determined fairly accurately by balancing it on a horizontal knife-edge. l is the distance from the centre of gravity to the top of the peg. The period T is obtained by timing a few hundreds of swings with a stop-watch, or by some special

labour-saving method. Experiment and graph both show that there are two values of l , when the point of support is on the same side of the centre of gravity, for which the period of oscillation is the same. AB and AC are two such lengths. Call them l_1 and l_2 respectively. Corresponding to the point B we have

$$T = 2\pi\{(k^2 + l_1^2)/l_1g\}^{1/2}, \quad \dots \quad (14)$$

and corresponding to C ,

$$T = 2\pi\{(k^2 + l_2^2)/l_2g\}^{1/2}. \quad \dots \quad (15)$$

Hence

$$gl_1T^2/4\pi^2 = k^2 + l_1^2$$

and

$$gl_2T^2/4\pi^2 = k^2 + l_2^2.$$

Subtracting, we have

$$T = 2\pi\{(l_1 + l_2)/g\}^{1/2}. \quad \dots \quad (16)$$

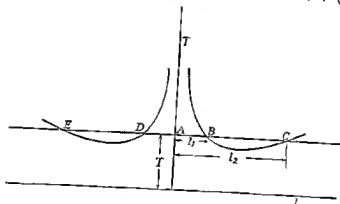


Fig. 5

On the other side of the centre of gravity there are two other points D and E , for which the period is the same (T). $AD = AB = l_1$, and $AE = AC = l_2$. Also $CD = BE = l_1 + l_2$. Thus C and D are two points, unsymmetrically placed with respect to the centre of gravity, whose distance apart is equal to the length of the simple pendulum whose period of oscillation is the same as that of the body, when the latter is oscillating about axes through C or D respectively. When the axis passes through C , C is called the *centre of suspension* and D the *centre of oscillation* or *centre of percussion*. When the axis passes through D , the names are interchanged.

6. Accurate Measurement of g at a Fixed Station (Clark).*

The best methods of measuring g at a given station involve the use of bar pendulums. Important early work on this subject was done by Prony (1800), Bohnenberger (1811), and particularly by Kater (1817). The latest refinements are to be found in researches by Heyl and Cook (1936) in America, and by Clark (1935-38) in England. A brief summary of Clark's work will now be given. The method involves an idea due to Bessel.

A rigid bar pendulum of special design is first made to describe small oscillations under gravity about a horizontal axis fairly near one end of the bar. The period of oscillation T is measured *in vacuo* and, as in equation (14),

$$T_1 = 2\pi\{(k^2 + l_1^2)/l_1g\}^{1/2}, \quad \dots (17)$$

where l_1 is the distance of the centre of gravity from the axis of rotation. Following Bessel, the bar pendulum is then inverted and allowed to describe small oscillations in a vertical plane about a second horizontal axis, on the opposite side of the centre of gravity and much closer to it than the first. In this position the period T_2 is measured and

$$T_2 = 2\pi\{(k^2 + l_2^2)/l_2g\}^{1/2}, \quad \dots (18)$$

where l_2 is the distance of the centre of gravity from the new axis. The second axis is so selected that T_2 and T_1 are very nearly equal, e.g. in a certain case $T_1 = 2.0057750$ sec. and $T_2 = 2.0057563$ sec. Squaring the values of T_1 and T_2 in equations (17) and (18), multiplying T_1^2 by l_1 and T_2^2 by l_2 , we get

$$T_1^2 l_1 = 4\pi^2(k^2 + l_1^2)/g,$$

$$T_2^2 l_2 = 4\pi^2(k^2 + l_2^2)/g.$$

On subtracting we find $T_1^2 l_1 - T_2^2 l_2 = 4\pi^2(l_1^2 - l_2^2)/g$ and hence

$$4\pi^2/g = (T_1^2 l_1 - T_2^2 l_2)/(l_1^2 - l_2^2). \quad \dots (19)$$

Using partial fractions this can be written in a form which proves much more useful than equation (19), namely

$$8\pi^2/g = (T_1^2 + T_2^2)/(l_1 + l_2) + (T_1^2 - T_2^2)/(l_1 - l_2). \quad (19a)$$

The advantage of this form of expression is that the second term on the right, which cannot be obtained accurately, is much smaller than the first term because, while $(T_1^2 - T_2^2)$ is nearly zero, $(l_1 - l_2)$ is about 50 cm.

The actual pendulum is a bar of a light paramagnetic alloy called

* Clark, *Phil. Trans. Roy. Soc. A*, Vol. 233, p. 63 (1940).

Y-alloy, consisting mainly of aluminium of I-section so as to combine strength with lightness. The ends are cut off square at about a metre apart (see fig. 6). Square slots are cut out of the middle of each end of the bar. Rectangular blocks of an alloy called delta metal, with their ends chromium-plated and lapped plane, are fitted tightly against the slotted ends and bolted on. The extra blocks form prolongations of the central part of the bar, but one is much longer than the other. The square holes left between the blocks and central bar permit the

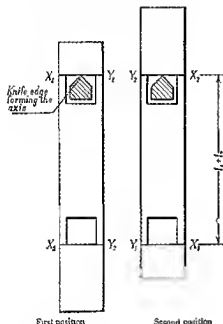


Fig. 6

bearing surfaces. It is measured by an optical interference method due to Sears and Barrell, involving a comparison with the known length of a standard end-gauge. In a typical case $l_1 + l_2 = 99.98997$ cm. at 20°C .

Whereas $l_1 + l_2$ is measured with extreme accuracy, the quantity $l_1 - l_2$ occurring in the second term of equation (19a) need only be determined to about a quarter of a millimetre. The reason is that the first term in equation (19a) is much larger than the second, e.g. in a typical case the value of the first is of the order 0.08 whereas the second is of the order 0.0000015, or two-hundred-thousandths of the first. The complete equation in this case is

suspension of the pendulum on a horizontal hard-steel knife-edge facing upwards and rigidly supported on an external stand. Thus a plane bearing surface of chromium-plated delta metal rests on the same steel knife-edge, forming the axis of rotation in both the first and second positions. The quantities T_1 , T_2 , $l_1 + l_2$ and $l_1 - l_2$ are those which are measured.

The periods T_1 and T_2 are measured with the pendulum, by means of a standard electrical chronograph reading to 0.0005 sec., the timing interval being of the order 12,000 sec.

The distance ($l_1 + l_2$) is the distance X_1X_2 or Y_1Y_2 between the plane

$$8\pi^2/g = 8.046127/99.98997 + 0.000073/47.89.$$

An error of half a millimetre in 47.89 cm., which is the value of $l_1 - l_2$ in this typical case, only causes a fractional error of about 2×10^{-5} in the value of g . Hence to determine $l_1 - l_2$ the separate values of l_1 and l_2 are found with sufficient accuracy by balancing the pendulum horizontally on a length of steel wire 3.6 mm. in diameter, and measuring the distances of the line of contact from the planes X_1Y_1 and X_2Y_2 with a metre steel scale. The above considerations relating to $l_1 - l_2$ reveal the advantage secured by the use of equation (19a) instead of equation (19).

Before insertion in equation (19a) four important corrections to the values of the periods T_1 and T_2 are made for (1) changes of temperature, (2) finite amplitude of swing, (3) non-uniformity of the rate of the standard clock, and (4) uncertainty in the interpretation of the records of the electrical chronograph. Two other corrections to T_1 and T_2 for (5) the finite radius of curvature of the knife-edges and (6) the effects of residual air in the experimental enclosure, are found to be much less important than the first four (see Table I). They are therefore not applied.

Four important corrections in the measured value of $l_1 + l_2$ are made for (7) elastic compression of the rod by the pressure of the knife edges, (8) compression of the rod by the residual air in the experimental enclosure, (9) yielding of the elastic support, and (10) the elasticity of the pendulum rod. The corrections

are gal. A thousandth of a gal is 1 milligal.

TABLE I.—FRACTIONAL CORRECTIONS TO THE VALUE OF g

(1) Temperature	$\pm 6 \times 10^{-3}$
(2) Amplitude	$\pm 3 \times 10^{-3}$
(3) Clock rate	$\pm 3 \times 10^{-3}$
(4) Uncertainty in chronograph records	$\pm 11 \times 10^{-3}$
(5) Finite radius of knife-edge	$< 4 \times 10^{-3}$
(6) Residual air	$< 5 \times 10^{-3}$
(7) Elastic compression by the knife-edge	$+ 5 \times 10^{-3}$
(8) Compression by the residual air	$+ 6 \times 10^{-3}$
(9) Elasticity of the support	$+ 15 \times 10^{-3}$
(10) Elasticity of the pendulum rod	$- 7 \times 10^{-3}$

Five readings of T_1 and five of T_2 form a set for the determination of one value of g . Eighteen such sets were obtained, giving a mean value of g of 981.1815 gal at a certain place in the National Physical Laboratory at Teddington.

7. Measurement of g at Sea.

It was formerly thought that the vibrations of ships prohibited the use of pendulums on board. The earlier methods of measuring g at sea,

such as those of Hecker and Duffield,* depend upon the simultaneous measurement of the atmospheric pressure P in two ways. The height of the column of mercury in a barometer tube gives H in the equation $P = g\rho H$, where g is the gravitational acceleration and ρ the density of mercury. A simultaneous measurement of the temperature at which water boils enables P to be obtained from tables of the temperatures and saturation pressures of water vapour. The point is that the second method of measuring P must not involve g . Alternatively, P can be measured by an aneroid barometer, or by causing a gas to exert a pressure equal and opposite to that of the atmosphere. Then $g = P/\rho H$. This method gives values of g with a probable error (see p. 293) of about ± 0.01 cm./sec.², which is relatively large compared with that obtained in pendulum experiments on land. The chief cause of this relatively large error is the so-called "bumping", that is, oscillations of the mercury in the barometer tube due to movements of the ship.

Vening-Meinesz † has devised a method which is far more accurate than that just described. He has shown that pendulum methods can be used on board ship, especially if the ship is a submerged submarine. Pendulums are subject to four disturbances due to the motion of the vessel and caused by

- (1) Horizontal acceleration of the point of suspension.
- (2) Vertical acceleration.
- (3) "Rocking", that is, the angular movement of the support.
- (4) Slipping of the knife-edges on the agate planes on which they rest.

By conducting experiments while the submarine is submerged, the total angular deviation due to the first three causes is kept below 1° , and the knife-edges do not slide on the agate planes. The horizontal acceleration has the greatest disturbing effect of the three. Its effect is completely eliminated by swinging two similarly made half-second pendulums (that is, pendulums whose full period is one second) together in the same vertical plane from the same support, but with different phases. If the pendulums are assumed to be isochronous (that is, having equal periods), the difference of the two angular displacements θ_1 and θ_2 gives an angle $\theta_1 - \theta_2$ which may be regarded as the angular displacement of a pendulum undisturbed by the horizontal acceleration of its support. For the equations of motion of the two pendulums may be written

$$M(k^2 + l^2)\ddot{\theta}_1 + Mgl\dot{\theta}_1 + A = 0$$

and

$$M(k^2 + l^2)\ddot{\theta}_2 + Mgl\dot{\theta}_2 + A = 0,$$

where A is a term representing the effect of the horizontal acceleration of the support, and is the same in the two cases. By subtraction,

$$M(k^2 + l^2)(\ddot{\theta}_1 - \ddot{\theta}_2) + Mgl(\dot{\theta}_1 - \dot{\theta}_2) = 0,$$

an equation from which any disturbing term is absent. The effect of the vertical accelerations of the point of support cannot be eliminated without eliminating

* Duffield, *Proc. Roy. Soc.*, Vol. 92, p. 505 (1916).

† Vening-Meinesz, *Geographical Journal*, Vol. 71, p. 144 (1928).

g itself. It appears, however, that the measured value of g is affected by the mean value of the vertical acceleration during the whole time of observation, and as the vertical movement is alternately up and down, fluctuating about the value zero, the mean value of the vertical acceleration is small. The corresponding error in g is made very small by making the duration of the observations very great. The third source of disturbance, rocking of the plane of oscillation, involves a small correction, which is easily computed from the recorded value of the rocking angle.

In practice, continuous photographic records are made, using three pendulums all swinging together from the same support. By an optical arrangement the sensitized paper, along
Thus two sets of values
pendulums are liable to

magnetic disturbances arising from the ferromagnetic structure and machinery of the submarine. Corrections for temperature effects are applied, although the apparatus is thermally insulated. The whole system is suspended in gimbals, and is thus screened from external shocks and effects due to small angular movements of the vessel. It is claimed that the probable error reached in a series of measurements conducted in a Dutch naval submarine proceeding in 1926-7 from Holland to Java via Panama is ± 0.0018 cm. per sec. per sec.

8. Relative Measurement of g .

When the values of g at various points in a country are to be compared with the value of g at some standard position, it is not usual

to employ the same technique as when an absolute measurement is contemplated. Suppose that the period of oscillation of one particular pendulum is measured, first at the standard position (T_0), and then at any other place (T_1). At the standard position $T_0 = 2\pi(l/g_0)^{1/2}$, where l is the length of the simple equivalent pendulum and g_0 is

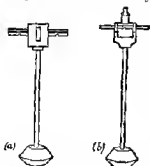


FIG. 7.—(From *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig).)

squaring, and rearranging, we have $g_1 = g_0 T_0^2 / T_1^2$, which gives the value of g_1 in terms of g_0 . In this manner a gravity survey is extended throughout

a country. Similar methods are in use in most countries; a brief account of the German method of experimenting is given here.

Half-second pendulums of a type invented by von Sternsok are used, that is, pendulums whose equivalent length is about 25 cm. and whose complete period is about one second. These are now made of the nickel-steel alloy invar, whose coefficient of linear expansion with temperature is extremely small. Figs. 7(a) and 7(b) show the general shape of two types of pendulum in common use, they differ only in the arrangement of the knife-edges. Four similar pendulums hang from the same massive support in four separate compartments of the apparatus,

The casing is made of mu-metal or some similar alloy, to screen the pendulums from magnetic fields. Oscillation experiments are conducted with three of these. The fourth is a "dummy" carrying a thermometer whose readings are assumed to give the temperature of the three experimental pendulums. In the latest form of apparatus the vessel housing the pendulums is evacuated, in order to eliminate du Buat's correction and other corrections.

Each pendulum carries an agate knife-edge, which rests on an agate plane on the support. The knife-edge forms the axis of oscillation when the pendulum swings. All the pendulums, except the dummy, carry a small plane mirror on their knife-edges, the normal to the centre of the mirror being in the plane of oscillation of the central line of the pendulum. The time of oscillation of each pendulum is determined by comparison with the time of oscillation of a standard clock or with signals from an accurate chronometer. For this purpose a method of coincidences is used. A small plane mirror is mounted on a fixed support so as to face the mirror on one of the experimental pendulums. It is parallel to that mirror when the pendulum is at rest. The standard clock or chronometer operates an electric relay, so that a horizontal electric spark is produced by breaking a certain circuit, once for every complete oscillation of the pendulum of the standard clock. An optical image of this spark, formed by rays of light reflected from each plane mirror in turn, is seen in the focal plane of the eyepiece of a telescope. The standard and experimental pendulums are so arranged that this image is seen in coincidence with the horizontal crosswire when the pendulums are "in phase" and each is passing through its rest-position. The mean interval between two coincidences is measured, over a period of about two hours. Let T_0 , τ_0 sec. be the periods of one complete oscillation of the experimental and standard pendulums respectively. T_0 is about 1.0 sec. and τ_0 is about 2.0 sec. Let the mean interval between coincidences be I sec. In I sec. let the standard pendulum make n complete oscillations. Then $n\tau_0 = I$. Let the experimental pendulum make N complete oscillations in the same time. Then $NT_0 = I$. It is known that T_0 is approximately equal to $\tau_0/2$, and we may write $T_0 = \tau_0/2 \pm \alpha$; then $I = N(\tau_0/2 \pm \alpha) = n\tau_0$, where α is a small period of time. Hence $2n\tau_0 = N(\tau_0 \pm 2\alpha)$ and $(2n - N)\tau_0 = \pm 2N\alpha$. Dividing both sides by τ_0 , we obtain $2n - N = \pm 2N\alpha/\tau_0$. Now $2n - N$ must be an integer, since n and N are both integers. Hence the least value of $2n - N$, other than zero, must be ± 1 , and the shortest interval I between two successive coincidences is that which makes $2n - N = \pm 1$. Hence $2N\alpha/\tau_0 = 1$. The equations $n\tau_0 = I = NT_0$ can be written in the form $n\tau_0 = I = (2n \pm 1)T_0$, whence $T_0 = I/(2n \pm 1) = I/(2I/\tau_0 \pm 1) = I\tau_0/(2I \pm \tau_0)$, which gives T_0 if τ_0 and I are known.

Various precautions are necessary in carrying out the experiment. (1) An automatic setting device is required, to place the knife-edge of the pendulum on the same part of the agate planes every time. (2) The agate planes need frequent repolishing. (3) They must be set horizontally before every experiment. (4) The support must be stable and free from tremors. (5) The deposition of dust and water vapour on the pendulum must be prevented. In a certain case water vapour altered T_0 by 3×10^{-6} sec.

The chief corrections to the measured value of T_0 are: (1) Correction for temperature variation; results are reduced to some standard temperature. (2) Corrections for air resistance and increased moment of inertia due to carried air; in the older technique results are reduced to the standard pressure 76 cm. of mercury; in the new vacuum apparatus these effects and corrections are eliminated. (3) Correction of T_0 to sidereal seconds. (4) Correction to zero amplitude; the initial amplitude does not exceed 1° . In recent work the standard clock is kept at a base station, and wireless signals are sent to the place of observation.

9. Variation of g with Time. Method of Tomaschek and Schaffernicht.

The "Bifilar Gravimeter" of Tomaschek and Schaffernicht * affords an accurate method of measuring minute temporal changes in the absolute value of g at a given place (figs. 8 and 9).

To a torsion head T is attached a long vertical spiral spring, made of wire of a special alloy (Krupp's Alloy W.T. 10) which is distinguished by the absence

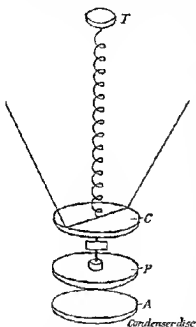


Fig. 8

of "creep" in its elastic properties. A flat circular disc C is attached to the lower end of the spring. Below the disc another disc P is suspended by means of a short wire. To opposite ends of a diameter of C are attached supporting fibres, forming a kind of bifilar suspension, which carries part of the weight of the system. When the torsion head is twisted through an angle θ , the disc C rotates in the same direction through an angle ϕ and finally comes to rest. Then the moment of the displacing couple due to the twisted spring is equal and opposite to the moment of the restoring couple due to the tension in the fibres of the bifilar suspension. The angles θ and ϕ increase together. If the disc C remained at the same level during the twisting, the moment of the restoring couple would increase to a maximum when ϕ was 90° , and would then diminish again as ϕ increased. The 90° position would be one of instability and the system would suddenly swing round through a large angle. In practice, on account of the raising of the disc and consequent alteration in the tension of the fibres, the position of instability is only reached when $\phi = 145^\circ$ approx. The spring is deliberately set so that this position is reached. Then when

the value of g alters, the weights of the two discs alter and the system rotates through a small angle. This angle is measured by means of the usual device of a mirror, lamp, and scale, the mirror being mounted on the wire between the two discs.

Figs. 9 (a) and (b) represent the disc C in equilibrium after a displacement ϕ . The moment of the restoring couple due to the tension T in the strings is twice the horizontal component of the tension in each, multiplied by the perpendicular distance z from the axis on to the line of action XY of the horizontal component. Hence

$$\text{Moment of restoring couple} = 2Tz\phi/l \quad (20)$$

* Tomaschek and Schaffernicht, *Ann. d. Physik*, Vol 15, p. 787 (1932).

opposite plate W_2 . The potential difference between W_1 and W_2 can be changed continuously, thus altering the downward force on W_1 .

The procedure by which changes in g are measured is as follows. The instrument is first set up at a given point, a certain p.d. V_1 is applied to the condenser W_1W_2 , and the circuit containing the condenser Y_1Y_2 is adjusted until the millimeter shows a suitable reading. The gravimeter is then moved to a new point, with the object of measuring Δg , the change in g . Suppose Δg to be positive, so that on moving to the new point the body X is pulled down slightly, and with it the plate Y_1 . The capacity of the upper condenser changes, and consequently the millimeter reading. By altering the p.d. between W_1 and W_2 , the force on W_1 is altered until the original millimeter reading is restored and X returns to its original position. Let the new p.d. between W_1 and W_2 be V_2 .

Δg is calculated by equating (a) the change in the weight of X due to shifting the instrument from the first to the second position to (b) the change in the attractive force on W_1 due to changing the p.d. from V_1 to V_2 . These two are equal since (b) compensates for (a). The change in weight of X is $M \cdot \Delta g$, where M is the mass. The attraction on W_1 in the first position is, as in the attracted-disc electrometer,

$$F_1 = 2\pi\sigma_1^2 A,$$

where σ = surface density in e.s.u. and A is the area of one face of W_1 . Hence

$$F_1 = 2\pi(Q_1/A)^2 A = 2\pi C^2 V_1^2 / A, \text{ since } Q_1 = CV_1.$$

When the potential is changed to V_2 the force becomes

$$F_2 = 2\pi C^2 V_2^2 / A,$$

and the difference is

$$F_1 - F_2 = 2\pi C^2 (V_1^2 - V_2^2) / A.$$

Thus when the value of g at the second point is greater than at the first we get the equation

$$M \cdot \Delta g = 2\pi C^2 (V_1^2 - V_2^2) / A.$$

$$\therefore \Delta g = 2\pi C^2 (V_1^2 - V_2^2) / A M.$$

Δg is therefore expressed in terms of quantities which are easily measured, viz. C , the capacity of the lower condenser; A , the area of one face of one plate; M , the mass of the suspended body X ; and the two potential differences, V_1 and V_2 .

By taking up to ten readings at each point it was estimated that the mean error in the value of Δg obtained as above was between 0.05 and 0.10 milligal.

The Gulf Gravimeter.

The purpose of the Gulf gravimeter is to measure changes in g , the gravitational acceleration, as the instrument is moved from one place to another. Thus it measures changes in g due to both horizontal and vertical displacements and gives $\partial g / \partial x$, $\partial g / \partial y$, and $\partial g / \partial z$. In this way ore bodies and oil deposits are revealed; in fact it was to find such deposits that this gravimeter was developed by the Gulf Research and Development Company of Pittsburgh, from 1932 onwards.

The instrument consists of a loaded and vertically suspended spiral spring (fig. 11) made not of circular wire but of metal ribbon of rectangular cross-section. The long side of the rectangle is vertical. The load is a simple weight attached centrally to the lower end. It therefore exerts a downward axial force, in the first place on the spring, and this, besides producing a downward linear extension, also causes a rotation about the vertical axis of the spring. Since the rectangular cross-section of the metal is very thin, the angle of rotation is large, and is such as to tend to uncoil the spring. When the instrument is set up at a certain place, the angle of rotation reaches an equilibrium value θ . On moving to a new place where g is different, the angle of rotation changes, and it is this change in the angle of rotation which is the quantity directly measured.

According to equation (39a), p. 69, the act of loading such a spring with a mass M grammes causes an angle of rotation

$$\theta = 3MgRl \sin \alpha \cos \alpha \{1/[n(1 - 3.361 \times 3b/16a)] - 4/q\}/16ab^2.$$

Hence on moving to a place where g changes to $g + \Delta g$, the angle changes from θ to $\theta + \Delta \theta$ and

$$\Delta g = 16ab^2 \cdot \Delta \theta / 3MlRl \sin \alpha \cos \alpha \{1/[n(1 - 3.361 \times 3b/16a)] - 4/q\}.$$

Also

$$\Delta g = g \cdot \Delta \theta / \theta.$$

The angle $\Delta \theta$ is measured by means of a beam of light falling on a plane mirror mounted on the axis of the spring and rotating with it. $\Delta \theta$ is magnified to $4\Delta \theta$ by the following arrangement (see fig. 12).

The movable mirror is the partially aluminized plane face NX of a plano-convex lens E_2 . Initially, i.e. at the first station, this mirror is parallel to the similarly aluminized plane face MK of a fixed plano-convex lens E_1 , a narrow air-gap lying between them. From a fine source of light S , which is at the focus of E_1 , a beam of light falls first on E_1 . The central ray of this beam SXP_2 strikes E_2 at X , and with the family of parallel rays goes on to P_2 , the focus of E_2 . On



Fig. 11.—Gulf gravimeter

moving the instrument to a second station where g is different, the spring, lens E_2 , and mirror rotate through $\Delta\theta$. In this case, some of the energy of the ray still forms an image at P_0 , but some is reflected along the path XK , KL . At L a further fraction of energy is transmitted through E_2 , and the family of such twice-reflected rays as KL forms an image at P_2 after being focused by the lens E_2 . A further family of rays such as MN is transmitted by lens E_2 after four reflections and is focused at P_4 . The deviation of SX , so as to give MN , is seen to be $4\Delta\theta$, and XP_4 is parallel to MN . This image P_4 , formed after four reflections, is the one selected in normal operations, and to give it maximum brightness, the aluminizing is arranged to have the optimum thickness, i.e. that which has a transmission coefficient of 12 per cent. P_4 is observed by a micrometer microscope reading to 0.0001 in. By using P_4 a value of Δg equal to 1 milligal produces a deflection P_0P_4 equal to 0.01 in. It is easy to read to 0.05 milligal.

The sources of error in the Gulf gravimeter are as follows:

(1) The creep, i.e. the slow change of reading with constant load. This can be reduced to a low value by a suitable choice of load, e.g. to 0.3 milligal per day over 30 days.

(2) Natural vibrations and "forced" vibrations due to ground unrest. These are reduced by electromagnetic damping.

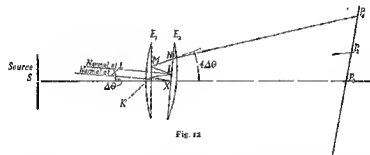


Fig. 12

(3) An error called "level sensitivity" in the form of a change of reading when the instrument is tilted slightly. This is small, since the top of the spring is the only point of support, and it is made very small by tapering the spring towards the top. Tilts of 10 seconds of angle (worst) to 60 seconds of angle (best) are required to cause an error of 0.1 milligal.

(4) Error due to temperature changes. Thermostatic control keeps the temperature constant to $\pm 0.01^\circ \text{C}$. even in field work.

The advantages of the Gulf gravimeter include:

(1) Simplicity of design and operation compared with the Eötvös balance.

(2) Greater sensitivity than pendulums, though less than Eötvös balance. Minimum $\Delta g/g$ measured by pendulums is 10^{-6} , by the Gulf gravimeter 10^{-7} , by the Eötvös balance 10^{-12} .

(3) Adjustability so as to measure values of Δg lying in ranges whose middle values are different, but whose extents are the same, e.g. in the range of 30 milligals between $g = 981,015$ and $980,985$ milligals, or in the range of 30 milligals between $g = 980,015$ and $979,985$ milligals. Adjustment is made by rotating the torsion head.

- (4) Constancy of calibration of readings over several years.
- (5) Rapid operation. Up to 100 readings, viz. at 100 stations, one mile apart, in 8 hours.
- (6) Easily adaptable for use on the bottom of the sea (Pepper type).
- (7) Not affected by magnetic fields.
- (8) No zero error because P_0 is read just before P_1 .
- (9) It measures the vertical as well as the horizontal gradients, whereas the Eötvös balance only measures the horizontal ones.

11. Changes of g with Direction. The Eötvös Torsion Balance.

It is possible to measure most accurately, not only the absolute value of g at any point, but also the rate of change of g with distance in any horizontal direction, and some other important quantities connected with the earth's gravitational field. These measurements are carried out with the Eötvös torsion balance, of which the theory will now be given. Take any point O on the earth's surface as an origin of co-ordinates. Let axes Ox , Oy , Oz be drawn, Ox towards the geographical north, Oy towards the east, and Oz downwards in the direction of the force of g at O , along Oz component.

field has a potential U at any point (x, y, z) and that at (x, y, z) the component forces on unit mass are $+\partial U/\partial x$, $+\partial U/\partial y$, and $+\partial U/\partial z$ respectively, which can be written in the form $\partial U/\partial x = g_x$, $\partial U/\partial y = g_y$, and $\partial U/\partial z = g_z$. At the origin $\partial U/\partial x = 0$, $\partial U/\partial y = 0$, $\partial U/\partial z = g_0$. The values of g_x , g_y , and g_z at any point (x, y, z) very close to the origin may be calculated by Maclaurin's theorem. Any function

$$f(x, y, z) = f(0, 0, 0) + x \frac{\partial f}{\partial x_0} + y \frac{\partial f}{\partial y_0} + z \frac{\partial f}{\partial z_0} + \text{smaller negligible terms,}$$

provided x , y , and z are small. The suffix 0 indicates that the values of the differential coefficients to be used are those at the origin. Hence

$$\begin{aligned} g_z &= g_0 + x \frac{\partial g_z}{\partial x_0} + y \frac{\partial g_z}{\partial y_0} + z \frac{\partial g_z}{\partial z_0} \text{ approx.} \\ &= 0 + x \frac{\partial^2 U}{\partial x_0^2} + y \frac{\partial^2 U}{\partial x_0 \partial y_0} + z \frac{\partial^2 U}{\partial x_0 \partial z_0}, \end{aligned} \quad (26)$$

since $g_x = \partial U/\partial x$, &c.

$$\text{Similarly, } g_y = 0 + x \frac{\partial^2 U}{\partial y \partial x_0} + y \frac{\partial^2 U}{\partial y_0^2} + z \frac{\partial^2 U}{\partial y \partial z_0} \quad (27)$$

$$\text{and } g_x = 0 + x \frac{\partial^2 U}{\partial x_0^2} + y \frac{\partial^2 U}{\partial x_0 \partial y_0} + z \frac{\partial^2 U}{\partial x_0 \partial z_0} \quad (28)$$

These are the forces per unit mass along Ox , Oy , Oz respectively, at the point x , y , z . Taking moments about the axis Oz , we see that the clockwise moment of forces acting on unit mass at (x, y, z) is $g_x x - g_y y$ (fig. 13). On a large body distributed over a certain space the clockwise moment is $\int (g_x x - g_y y) dm$, where dm is the mass concentrated at any point (x, y, z) and the integral sign simply indicates the summation over all the elements of mass in the body.

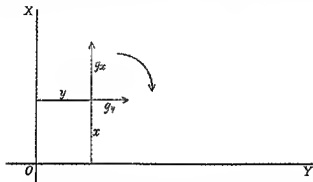


Fig. 13

One of the common forms of the Eötvös balance (fig. 14) involves the above theory. The principal part is a torsion head from which hangs a thin torsion wire, usually of a platinum-iridium alloy, about 30×10^{-3} to 40×10^{-3} mm. in diameter and 25 to 60 cm. in length. This carries a horizontal rectangular beam of aluminium about 40 cm. long. One end of this beam carries a cylindrical weight of platinum, gold, or silver of mass about 30 gm., with its axis horizontal. From the other end of the beam hangs a cylindrical weight of mass about 25 gm., supported by a platinum-iridium wire about 40 cm. long. This suspension system carries a small plane mirror just above the level of the beam. The system, regarded as a whole, forms a body acted on by a torque whose moment is given by the above expression. Let the origin O of co-ordinates be the mid-point of the beam. The moment of the torque is $\int (g_x x - g_y y) dm$, and the integral is to be taken over the whole of the suspension system. If we substitute for g_x and g_y from equations (26) and (27), the moment becomes

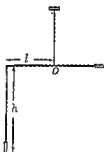


Fig. 14

$$\begin{aligned} & \left(\frac{\partial^2 U}{\partial y^2} - \frac{\partial^2 U}{\partial z^2} \right) \int xy dm + \frac{\partial^2 U}{\partial x \partial y_0} \int (x^2 - y^2) dm \\ & + \frac{\partial^2 U}{\partial y \partial z_0} \int xz dm - \frac{\partial^2 U}{\partial x \partial z_0} \int yz dm \quad \dots \quad (29) \end{aligned}$$

In experiments with the Eötvös torsion balance the suspension system is released and takes up some position of equilibrium in which the axis of the beam,

though horizontal, makes an angle α , called the azimuth angle, with Ox , and $90 - \alpha$ with Oy . In order to use the above expression for the moment of gravitational axes of beam, ζ points to From Fig. 15,

$$x = \xi \cos \alpha - \eta \sin \alpha,$$

$$y = \xi \sin \alpha + \eta \cos \alpha.$$

Then

$$\int xy \, dm = \frac{1}{2} \sin 2\alpha \int (\xi^2 - \eta^2) \, dm + \cos 2\alpha \int \xi \eta \, dm,$$

$$\int (x^2 - y^2) \, dm = \cos 2\alpha \int (\xi^2 - \eta^2) \, dm - 2 \sin 2\alpha \int \xi \eta \, dm,$$

$$\int xz \, dm = \cos \alpha \int \xi z \, dm - \sin \alpha \int \eta z \, dm,$$

and

$$\int yz \, dm = \sin \alpha \int \xi z \, dm + \cos \alpha \int \eta z \, dm.$$

The suspension system is so constructed that its mass is symmetrically distributed with respect to the axis $O\xi$ and also the vertical plane ξOz (Fig. 16). Symmetry with respect to the axis $O\xi$ makes $\int \xi \eta \, dm = 0$, for it means that for

it, $\int \xi z \, dm = 0$, because the integral can be split up into pairs of terms of the form $+\xi z \, dm$ and $-\xi z \, dm$, which add up to zero. The lower weight and wire contribute an amount nil to the integral $\int \xi z \, dm$.

for $\int \eta z \, dm = 0$, for it can be divided into pairs of terms of the form $+\eta z \, dm$ and $-\eta z \, dm$, which add up to zero. In the remaining integral $\int (\xi^2 - \eta^2) \, dm$, $\eta^2 \ll \xi^2$ for most elements of mass. Hence $\xi^2 - \eta^2 = \xi^2 \pm \eta^2$, very nearly, and as

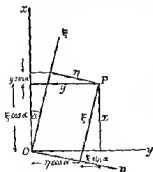


Fig. 15



Fig. 16

$\int (\xi^2 + \eta^2) \, dm = K$, the moment of inertia of the suspension system about Oz , $\int (\xi^2 - \eta^2) \, dm = K$, to a close approximation. On substituting the results just

obtained in the expression (29) for the moment of the gravitational forces, the moment becomes

$$\frac{1}{2} K \sin 2\alpha \left(\frac{\partial^2 U}{\partial y_0^2} - \frac{\partial^2 U}{\partial x_0^2} \right) + K \cos 2\alpha \frac{\partial^2 U}{\partial x \partial y_0} + m h \left(\cos \alpha \frac{\partial^2 U}{\partial y \partial z_0} - \sin \alpha \frac{\partial^2 U}{\partial x \partial z_0} \right). \quad (30)$$

This moment tends to displace the torsion system. A restoring torque, whose moment is $c\theta_\alpha$, is called into play in the suspending wire; c is the torsional constant and θ_α is the angular displacement from the position when there are no torques acting. When the system is at rest, the displacing and restoring moments are equal. The usual mirror, lamp, and scale are used to measure deflections. Let π_α be the scale reading corresponding to the displacement θ_α , π that corresponding to zero displacement, and D the distance between mirror and scale. Then $\pi_\alpha - \pi = 2D\theta_\alpha$ and $c\theta_\alpha = c(\pi_\alpha - \pi)/2D$. The equality of displacing and restoring moments is represented by the equation

$$\pi_\alpha - \pi = DK(U_{yy} - U_{xx}) \sin 2\alpha/c + 2KD U_{xy} \cos 2\alpha/c \\ + \{2Dmh/c\}(U_{yz} \cos \alpha - U_{xz} \sin \alpha), \quad (31)$$

where $U_{yy} = \partial^2 U/\partial y_0^2$, $U_{xx} = \partial^2 U/\partial x_0^2$, $U_{xy} = \partial^2 U/\partial x \partial y_0$, $U_{yz} = \partial^2 U/\partial y \partial z_0$, and $U_{xz} = \partial^2 U/\partial x \partial z_0$. This can be written in the form

$$\pi_\alpha - \pi = P \sin 2\alpha + Q \cos 2\alpha + A \sin \alpha + B \cos \alpha, \quad (32)$$

where π , P , Q , A and B are five unknowns and π_α and α are two experimentally measurable quantities. In general, to determine five unknowns, five equations are required. This involves five separate readings of π_α for five separate values of the azimuth angle α . In practice, the procedure is simplified by taking readings in six azimuths, in which $\alpha = 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ$ and 300° respectively. π_α is read by a telescope carried on an arm fixed to the case of the instrument. The same arm carries the scale, graduated in half-millimetres, whose image is seen in the mirror. π , the reading corresponding to the unknown position of zero torque, is, of course, not obtainable directly. Calculation gives π , P , Q , A and B . Then, at the origin,

$$U_{yy} - U_{xx} = Pc/DK, \quad (33)$$

$$U_{xy} = Qc/2DK, \quad (34)$$

$$U_{xz} = -Ac/2Dmh, \quad (35)$$

$$U_{yz} = Bc/2Dmh. \quad (36)$$

These are the four quantities usually measured at any point. U_{xx} and U_{yy} are, of course, the same as $\partial g/\partial x_0$ and $\partial g/\partial y_0$, the rates of change of g in horizontal directions near the origin. The other two quantities represent quantitative properties of the gravitational field near the origin. $U_{xz} = \partial g/\partial z_0$ is not measured by this apparatus.

The quantity c is determined by applying a known displacing couple G to the system and measuring the angle ϕ produced. Then $c = G/\phi$. K is determined by an oscillation experiment; m , D , h and l are found by ordinary weighing and length-measuring methods.

12. The Gravity Gradient and Horizontal Directive Tendency.

In connexion with gravitational surveys and the construction of maps indicating the results, it has been found convenient to introduce two other quantities connected with the earth's gravitational field and with the expressions in equations (33), (34), (35) and (36). These are called the *gravity gradient* and the *horizontal directive tendency* respectively.

The term gravity gradient is an abbreviation for "maximum gradient of g in a horizontal direction near a point", where g is $\partial U/\partial z$, the vertical gravitational intensity at the point. The gravity gradient is therefore equal to $\partial g/\partial s$, the rate of variation of g per unit of length measured in the direction of maximum rate of change of g ; it is a vector quantity. Let $\partial g/\partial s$ make an angle ϕ with Ox and Oy be $\partial g/\partial x$ and $\partial g/\partial y$. Then $\partial g/\partial s = \sqrt{(\partial g/\partial x)^2 + (\partial g/\partial y)^2}$. Writing $g = \partial U/\partial z$, $\partial g/\partial x = \partial^2 U/\partial x \partial z = U_{xz}$. Denote we have

$$\text{and } \left. \begin{aligned} U_{xz} &= G \cos \phi \\ U_{yz} &= G \sin \phi \end{aligned} \right\} \quad \dots \quad (37)$$

$$\text{or } G = (U_{xz}^2 + U_{yz}^2)^{1/2} \quad \dots \quad (38)$$

Hence G can be calculated if we know U_{xz} and U_{yz} which may be derived by experiments with the Eötvös torsion balance as on p. 30.

The horizontal directive tendency (H.D.T.)* at any point is a directed quantity but not a true vector. It is given by $R = g(1/a_1 - 1/a_2)$, where g has its usual meaning and a_1, a_2 are the maximum and minimum radii of curvature of the gravitational equipotential or level surface at the point. Its direction is conventionally assumed to be that horizontal direction in which the vertical downward curvature of the level surface is least and the radius of curvature greatest. Let its direction make an angle θ with Ox . It can be shown that R is related to the differential coefficients in equations (33), (34), (35) and (36), as follows:

$$R \sin 2\theta = 2U_{xy} \quad \dots \quad (39)$$

$$R \cos 2\theta = U_{xx}^2 - U_{yy}^2 \quad \dots \quad (40)$$

Rankine has shown that equation (31) may be transformed by the aid of substitutions from equations (39) and (40) into the form

$$n_s - n = (DKR/c) \sin 2(\theta - \alpha) + (2DmkhG/c) \sin(\phi - \alpha). \quad (41)$$

This form brings out the separate importances of G and R , and indicates what features must be possessed by torsion balances suitable for the

* Ger. Krümmungsgrosse.

measurement of G or R separately. In survey maps, G is represented in magnitude and direction by an arrow drawn from the point P which possesses this value of G . R is represented in direction and magnitude

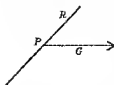


Fig. 17

by a straight line without any pointed or feathered end, drawn through P (fig. 17). Curves joining those points on a level surface, where g has equal values, are called *isogams*. G is always directed along a normal to an isogam. The dimensions of both G and R are those of $(\text{time})^{-2}$, and they are usually expressed in the so-called Eötvös units. One Eötvös = $10^{-9} \text{ sec.}^{-2}$. With

a well-made Eötvös balance, a deflection of one scale division corresponds to a change of about one Eötvös unit. Measurements of G , R , and other quantities are now employed commercially in the detection of heavy ores. The Kursk region of Russia, in longitude $36^{\circ} 52' \text{ E.}$, offers an example of an extensive region in which both the gravitational and the magnetic fields of the earth show very marked anomalies.

13. Alteration in Direction of the Force of Gravity with Time. The Horizontal Pendulum.

A problem which has recently received much attention is that of finding the change in direction, as time goes on, of the force of gravity at a point on the earth's surface. This is equivalent to finding the change in direction of a plumb-line. The point of support of a plumb-line is attached firmly to the earth and moves with the earth's surface, and a plumb-line sets itself normal to a gravitational equipotential surface. Hence deformations of the earth's surface and of the equipotential surface cause changes in the direction of a plumb-line. As these changes amount at most to 0.1 second of angle, their direct determination with a plumb-line is out of the question.

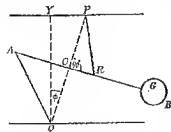


Fig. 18

Perhaps the commonest instrument used to measure temporal changes in the direction of the force of gravity is the horizontal pendulum, said to have been devised in 1832 by Hengler. In principle this instrument (fig. 18) consists of a rod AB , supported in an inclined position by two light strings AQ and PR , attached to rigid supports at P and Q . The straight line PQ makes an angle ϕ with the direction

of the force of gravity. The rod AB takes up a position of equilibrium in a certain plane, which is parallel to the force of gravity, as shown

in fig. 18. When AB is slightly displaced laterally, for example, if B is drawn towards the observer and released, the pendulum describes slow small oscillations, whose period may be calculated as follows.

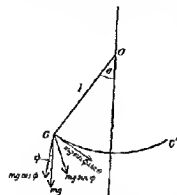


FIG. 19

The centre of gravity G of the pendulum describes a circular arc GG' (fig. 19) as the pendulum oscillates. The centre of this circle is O , the point where AB crosses PQ .

restoring force on the pendulum when it has rotated through a small angle θ in the inclined plane. At G there is a force mg acting in the direction of gravity. This may be resolved into two components. (1) $mg \cos \phi$ in a direction perpendicular to the inclined plane in

which the pendulum rotates, and (2) $mg \sin \phi$ in the inclined plane of rotation of the pendulum. The force $mg \sin \phi$ may be further resolved into two components, along and perpendicular to OG . The component $mg \sin \phi \sin \theta$, perpendicular to OG , is important here, as it is the force which restores the pendulum to its initial position. Its moment about the inclined axis is $mg l \sin \phi \sin \theta$, where $OG = l$. When θ is small this becomes $mg l \sin \phi \cdot \theta$. The equation of motion of the pendulum about the inclined axis PQ is therefore $mk^2 \ddot{\theta} + mg l \sin \phi \cdot \theta = 0$, where mk^2 is the moment of inertia and frictional or viscous forces are neglected. Hence the period of oscillation is

$$T = 2\pi(k^2/gl \sin \phi)^{1/2}. \quad (42)$$

In practice ϕ is made very small, so that T is very great. When $\phi \rightarrow 90^\circ$, $T = T_{90} = 2\pi(k^2/gl)^{1/2}$. Hence

$$T/T_{90} = (1/\sin \phi)^{1/2} \quad \text{and} \quad \sin \phi = (T_{90})^2/T^2 \quad (43)$$

Oscillation experiments give T_{90} and T , whence $\sin \phi$ and ϕ are calculated

$PP' = PQ \cdot d\delta$, where $d\delta$ is the change in direction of gravity required. Hence $d\delta = \sin \phi \cdot dB = (T_{90})^2 dB/T^2$, by equation (43). In practice it is the angle dB

which is measured. This is done by means of the usual mirror, lamp, and scale. T and $T_{30'}$ are measured as before by oscillation experiments, so that dA can be calculated.

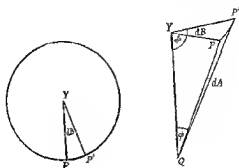


Fig. 20

Another method of finding the change of direction of gravity in a perpendicular plane is to mount two horizontal pendulums inside one case, so set that by the first method one gives $\phi = \phi_1$, and the other $\phi = \phi_2$, in two perpendicular azimuths. In very accurate measurements by Schweydar $T_{30'} = 0.435$ sec., $T =$ about 15 sec., and on the scale measuring dA , a deflection of 1 mm. corresponds to a value of dA of 0.022 sec. of angle.

CHAPTER III

The Newtonian Constant of Gravitation

1. Newton's Law of Gravitation.

According to Newton's law of gravitation, every particle of matter in the universe attracts every other particle with a force which is proportional to the mass of each particle concerned and inversely proportional to the square of their distance apart. In symbols, the law may be written

$$F = G \frac{m_1 m_2}{d^2}, \quad \dots \dots \dots (1)$$

where F is the force of attraction between the particles, m_1 and m_2 are their masses, and d is their distance apart. G is a constant known as the Newtonian constant of gravitation, whose dimensions are $+3$ in length, -1 in mass, and -2 in time.

Astronomical measurements prove that, except where relativistic corrections are appreciable, the law holds even when d is very great. Since two different atoms cannot be absolutely superposed on one another, it would seem that a repulsive force must come into play between two atoms, when d is of the order 10^{-7} cm., and that Newton's law then ceases to hold. (Actually, conditions are complicated by electrical forces which result from the ultimate electrical nature of matter.) For all greater values of d it appears to be true. Further, if the index of d is written in the form $2 + k$, $k \leq 1.5 \times 10^{-2}$, that is, $k = 0$ within the limits of experimental error.

It is proved in Ex. 2, p. 312, that a sphere or spherical shell of homogeneous attracting matter made up of particles obeying Newton's law exerts, as a whole, an attraction upon an external particle as if the whole mass of the sphere or shell were concentrated at the centre. Thus the attraction of a sphere of mass M gm. on a particle of mass m gm. situated R cm. from the centre of the sphere and outside it is GMm/R^2 dynes. This applies if the sphere is (a) uniform throughout or (b) composed of homogeneous spherical shells. To a first approximation we may regard the earth as a sphere of mass M , though there are actually many parts of the earth, the crust, the mantle, the core, etc. Moreover, the shape of the earth's surface is not exactly spherical, but is

that of a spheroid with its minor axis in the direction of the earth's geographical axis. Neglecting these points, we see that owing to the earth's attraction a particle placed at a point on the surface will move, if free, towards the centre of the earth. If we denote the acceleration by g and the mass by m , the attractive force is mg , by Newton's second law of motion. It is also GMm/R^2 , by the law of gravitation. Hence $GMm/R^2 = mg$ and

$$\frac{GM}{R^2} = g. \quad \dots \dots \dots (2)$$

If ρ is the mean density of the earth and R its radius, $M = 4\pi R^3 \rho / 3$, and, eliminating M from (2), we obtain

$$g = \frac{4}{3}\pi GR\rho. \quad \dots \dots \dots (3)$$

This relation contains four quantities, G , g , R , and ρ , and may be used to calculate any one of them, provided the other three are known. The present chapter will be mainly concerned with experimental determinations of G . The value of ρ can be calculated if g , G , and R are known. Equation (2) may also be used to determine G if a value of M , derived by astronomical methods, is assumed.

The gravitational constant has been measured experimentally by (a) large-scale experiments and (b) laboratory experiments. Of the former, which are now of historical interest only and in which the earth is one of the attracting masses, may be mentioned (a) Bouguer's measurements in Peru of the relative masses of a mountain (whose mass was estimated from its volume and density) and the earth from the deflection of a plumb-line placed near the mountain, (b) experiments of Airy and others on the relative masses of a spherical shell of the earth (whose mass was estimated from its volume and density) and the entire earth, from observations of the times of oscillation of a pendulum at the bottom of a mine shaft and at ground level respectively.

2. Measurement of G . Boys' Method.

Perhaps the most important methods of measuring G are those in which a torsion balance is used. The original type of apparatus, designed by Michell, has been improved by Cavendish, Cornu, and others, particularly by Boys (1889). The delicate torsion balance used by Boys consists, first, of a central vertical fibre of quartz, suspended from a metal disc called the torsion bead. The fibre carries a horizontal glass beam; from grooves in both ends other quartz fibres of unequal length hang vertically, each supporting a small gold sphere. This suspension system is hung inside a glass tube, of internal diameter about 3.8 cm., and is thus protected from draughts. Further, the air pressure inside can be adjusted to any required value. Outside the

tube two equal spheres of lead about 10.8 cm. in diameter are suspended at equal distances from the axis. The centres of these spheres are respectively situated in the same horizontal planes as the centres of the gold balls, that is, they are at different levels. Each lead sphere exerts an attraction on each gold sphere, but by having the two different levels, the attraction of a lead sphere on that gold sphere whose centre is on a level with its own is made far greater than that on the other. The effect of the attractions is to produce a torque about the axis, and the central fibre is twisted through an angle θ . The suspension system comes to rest when the resultant moment of the displacing forces due to gravitational attraction is equal and opposite to the moment of the restoring forces called into play in the twisted fibre. The position of the centres of the lead spheres is chosen so as

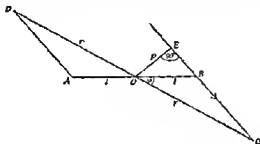


Fig. 1

to make the moment of the displacing forces as large as possible. The angular deflection θ is obtained by use of a mirror, lamp, scale and telescope, the mirror being the horizontal glass beam itself. The large spheres are then moved to new and similar positions on the opposite sides of the gold spheres, so as to produce a maximum displacing moment in the opposite direction, and the change in scale reading is that which is actually read.

The value of G is calculated as follows. Let M , m represent the masses of the two kinds of spheres respectively. In fig. 1, which represents a plan of the system after equilibrium has been reached, A , B represent the centres of the gold spheres, and C , D those of the lead spheres respectively. The attractions between

$$2GMmlr \sin \varphi / EC^2 = 2GMmlr \sin \varphi / (l^2 + r^2 - 2lr \cos \varphi)^2.$$

The moment of the restoring forces is $c\theta$, where c is the torsional constant of the

central quartz fibre and θ is the angular deflection of the suspension system from its equilibrium position. Hence

$$G = c\theta(p^2 + r^2 - 2lr \cos \phi) / 2Mmb \sin \phi. \quad (4)$$

As θ corresponds to one-half of the change in the scale reading when the large spheres are moved from the first position to the second, it is calculated by dividing the change in the scale reading by four times the distance from the scale to the mirror. The torsional constant c is obtained by measuring T , the period of the natural oscillations of the suspension system in the absence of the large masses. $T = 2\pi(I/c)^{1/2}$, where I is the moment of inertia of the suspension system about its axis, a quantity which can be obtained by measurements of its mass and linear dimensions.

The value of G obtained by Boys is 6.653×10^{-8} c.g.s. units, which corresponds to a mean density of the earth of 5.527 gm. per c.c. The probable error is not calculated by Boys. A few dimensional details are appended. In one experiment the length of the central quartz fibre is 43.2 cm., and its diameter is about 0.0125 mm.; the beam is 23 mm. long, the scale is 700 cm. from it and is divided into half-millimetres. The large spheres have masses of about 7407 gm., and the small ones of 2.85 gm. The difference in level is about 15 cm. The scale deflection corresponding to a rotation of $\theta_1 + \theta_2$ is 18.48 cm. The angle BOC is $64^\circ 38'$. The distance CD is 15 cm. The period of oscillation T is about 96 sec.

The principal advantage introduced by Boys is the use of thin quartz fibres, which are extremely sensitive and which retain their elastic properties. The great reduction in the dimensions of the apparatus which is thus rendered possible (1) eliminates the difficulty of convection currents arising from unequal temperatures of different parts of the bulky apparatus, (2) enables the size of the cumbersome lead attracting spheres to be reduced.

3. Measurement of G . Heyl's Method.

Probably the most accurate value of G hitherto obtained is that of Heyl* (1930). He uses the "time of swing method" formerly used by Braun. The suspension system of a torsion balance, consisting of two small equal spheres hanging with their centres at the same level, is allowed to describe small oscillations in the gravitational field of two large masses, whose centres of gravity are also at the same level. The large masses are placed in two separate positions, represented in plan in fig. 2. The two small masses are placed with their centres at the same level, because of the greater precision possible in the important measurement of the distance between the centres. The accuracy is improved, as compared with Braun's work, by using very heavy large masses of about 66.3 Kgm. each.

The theory of the experiment, when the large masses are in the "near" position, may be discussed with reference to fig. 3. Consider the total energy of the suspension system when the centres of the small masses are in the displaced positions C, D . The equilibrium

* Heyl, *Bureau of Standards Journal of Research*, Vol. 5, p. 1243 (1930).

positions are at A and B . The centres of the large masses are fixed at X and Y . The total energy is made up of (1) kinetic energy equal to $I\dot{\theta}^2/2$, where I is the moment of inertia of the suspension system about its vertical axis of symmetry, and θ is the angular displacement; (2) potential energy due to torsion of the fibre, equal to $k\theta^2/2$, where

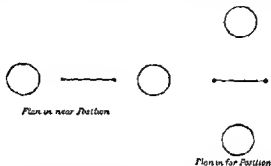


Fig. 2

k is the torsional constant of the fibre; (3) potential energy due to the proximity of the large and small masses, that is, due to the fact that D is near X and Y , and that C is also near X and Y . The large masses are vertical steel cylinders, and the evaluation of the gravitational potential at D and C respectively, due to a cylinder whose centre of gravity is at X or Y , involves zonal harmonics and is beyond the scope of this book. The final expression for the gravitational potential

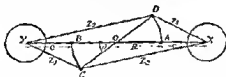


Fig. 3

energy of the whole displaced suspension system may, however, be written in the form $GA_1\theta^2/2$. A_1 is the product of one large mass and one small mass and a purely geometrical function of R and c , where $R = OA$, $c = AX$, and G is the Newtonian constant sought. If friction is neglected, the total energy is a constant. Hence

$$I\dot{\theta}^2/2 + k\theta^2/2 + GA_1\theta^2/2 = \text{a constant.}$$

On differentiating with respect to time and dropping the factor $\dot{\theta}$, we have

$$I\ddot{\theta} + (k + GA_1)\dot{\theta} = 0.$$

representing an oscillation whose period, uncorrected for small errors, is

$$T_1 = 2\pi\{I/(k + GA_1)\}^{\frac{1}{2}}. \quad (5)$$

Here k as well as G is regarded as unknown; A_1 is calculated from the geometry of the system. In a similar way, when the large masses are moved to the "far" position, and the torsion pendulum again describes small oscillations, its equation of motion is $I\ddot{\phi} + (k + GA_2)\phi = 0$, where A_2 is the new geometrical constant which replaces A_1 . The uncorrected period of oscillation is

$$T_2 = 2\pi\{I/(k + GA_2)\}^{\frac{1}{2}}. \quad (6)$$

On eliminating k from equations (5) and (6), and solving for G , we have

$$G = 4\pi^2 I (T_2^2 - T_1^2) / (A_1 - A_2) T_1^2 T_2^2. \quad (7)$$

As regards experimental details, the large masses are cylinders of forged and machined steel, of mass about 66.3 Kgm. each, suspended from a supporting system capable of rotation about a vertical axis, midway between them. In three sets of experiments the small masses are pairs of gold, platinum, and optical glass spheres respectively, in each case of mass about 50 gm. They are suspended from a very light torsion system, consisting of (1) a torsion wire of tungsten about 1 m. long and 0.025 mm. in diameter, (2) a separating rod of aluminium 20.6 cm. long and of mass 2.44 gm., (3) various supporting wires as shown in fig. 4. Over 90 per cent of the moment of inertia is in the small spheres themselves. This system is enclosed in a large brass container resting on a plate-glass base. The air pressure within is reduced to about 2 mm. of mercury. The usual arrangement of mirror, lamp, scale and telescope is used to observe the oscillations, which are started by bringing bottles of mercury near the small spheres and then removing them. Transits of lines on the image of a scale on glass, across the vertical crosswire of the telescope, are noted by an observer and recorded on one pen of a two-pen chronograph. The other pen records seconds signals from a standard clock.

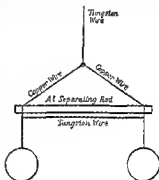


FIG. 4

The gold balls are found to absorb mercury vapour from the air of the laboratory. Hence their mass increases by about 0.138 gm. in 49 gm. in seven months. Results obtained with them were discarded. With varnished platinum balls the value obtained, as the mean of five results, is $G = 6.664 \times 10^{-6}$ c.g.s. units, and with glass balls, as the mean of five results, $G = 6.674 \times 10^{-6}$ c.g.s. units. The mean of the means is 6.669×10^{-6} c.g.s. units, as compared with 6.658×10^{-6} in Boys' and Braun's experiments. The cause of the differing results with platinum and glass balls is not accounted for, though it has been proved that this is not directly due to the differing natures of the materials.

4. Measurement of G . Zahradnick's Resonance Method.

The apparatus* used consists of two coaxial torsion balances, the axes being vertical. For the sake of brevity they are called primary and secondary. The primary balance is relatively robust and consists of a central steel wire with a beam in the form of \sqcap , made of brass tubing. Heavy equal lead spheres are mounted at the same level, near the ends of the vertical arms (fig. 5). The secondary balance is smaller,

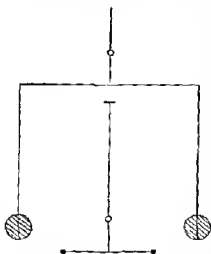


Fig. 5

and its axis is vertically below that of the primary. Its beam is simply a horizontal piece of aluminum wire with small equal lead spheres at the ends. Each suspension wire carries a mirror and has its own lamp, and the oscillations of each balance are registered photographically on a drum covered with sensitized paper. The rest-positions of the two balances are adjusted to be in the same vertical plane, and each balance when displaced and released describes damped harmonic oscillations about its rest-position, since the two systems exert gravitational forces and couples on each other. The damping of the primary balance is exceedingly small. To exclude draughts, the secondary bal-

ance is enclosed in a wooden case inside the case protecting the primary balance. The experiment consists in the adjustment of the two systems until the condition of resonance is established, that is, until the two periods of oscillation are equal. An equal number of turning points of both systems are noted. Then the masses and linear dimensions of each balance being known, G can be calculated.

The theory is as follows. Take the central point of the secondary beam as origin (fig. 5). Let Ox be horizontal and in the rest-position of the axis of the beam, Oy horizontal and perpendicular to Ox , Oz vertical and upwards. When the secondary beam is displaced through an angle ϕ , let the co-ordinates of the centres of the small spheres (mass m_1) be $x_1 = R_1 \cos \phi$, $y_1 = R_1 \sin \phi$, $z_1 = 0$, and $-x_1$, $-y_1$, 0 respectively. When the primary beam is displaced through an angle ψ ,

* Zahradnick, *Phys. Zets.*, Vol. 34, p. 126 (1933).

and when ϕ and ψ are sufficiently small, this becomes

$$2Gm_1m_2R_1R_2\Delta(\psi - \phi),$$

where

$$\Delta = 1/\{(R_1 - R_2)^2 + c^2\}^{\frac{1}{2}} - 1/\{(R_1 + R_2)^2 + c^2\}^{\frac{1}{2}}.$$

Let the differential equation of motion of the secondary system, in the absence of the primary, be

$$K\ddot{\phi} + P\dot{\phi} + D\phi = 0.$$

When the above moment is acting, this becomes

$$K\ddot{\phi} + P\dot{\phi} + D\phi = 2Gm_1m_2R_1R_2\Delta(\psi - \phi) = E(\psi - \phi), \quad (10)$$

say, where

$$E = 2Gm_1m_2R_1R_2\Delta. \quad . \quad . \quad . \quad (11)$$

Then

$$K\ddot{\phi} + P\dot{\phi} + \bar{D}\phi = E\psi,$$

where

$$\bar{D} = D + E.$$

Assume that ψ corresponds to an undamped simple harmonic oscillation, $\psi = \psi_0 \cos \omega_2 t$ (for, as we have assumed above, the damping of the primary system is very small). Then

$$K\ddot{\phi} + P\dot{\phi} + \bar{D}\phi = E\psi_0 \cos \omega_2 t$$

The particular integral of this is the important part of the solution, and is obtained by the use of operators or otherwise. It is

$$\phi = \phi_0 \cos(\omega_2 t - \epsilon),$$

where

$$\phi_0 = E\psi_0/K\{(2\delta\omega_2)^2 + (\omega_0^2 - \omega_2^2)^2\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad (12)$$

$$\tan \epsilon = 2\delta\omega_2/(\omega_0^2 - \omega_2^2), \quad . \quad . \quad . \quad (13)$$

and

$$\delta = P/2K, \quad \omega_0^2 = \bar{D}/K. \quad . \quad . \quad . \quad (14)$$

Resonance occurs when ϕ_0 is a maximum as ω_2 varies. By differentiation, this occurs when $2\delta^2 = \omega_0^2 - \omega_2^2$, that is, when

$$\phi_0 = E\psi_0/2K\delta\{\omega_2^2 + \delta^2\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (15)$$

Here ϕ_0 and ψ_0 are the amplitudes corresponding to the case of resonance. We now replace E by $2Gm_1m_2R_1R_2\Delta$ and rearrange. We then obtain

$$G = \phi_0 K \delta \{\omega_2^2 + \delta^2\}^{\frac{1}{2}} / \psi_0 m_1 m_2 R_1 R_2 \Delta. \quad . \quad . \quad . \quad (16)$$

The value of ϕ_0/ψ_0 is obtained from a number of observed turning points of both systems; K is the moment of inertia of the secondary balance; $\omega_2 = 2\pi/T_2$, where T_2 is the period of oscillation; $\delta = 2\lambda/T_1$, where λ is the logarithmic decrement, and T_1 the natural period of the secondary in the absence of the primary. R_1 , R_2 and Δ are obtained from the linear dimensions of the apparatus. An important correction is applied for the attraction on parts of the secondary balance other than the masses m_1 , e.g. the beam, due to the masses m_2 . A small correction is required for the slight damping of the primary balance. Zahradnicek gives $G = 6.659 \pm 0.02$ as the value derived from seven experiments. The method seems to be very accurate. It has the advantage that a large number of values can be obtained in a relatively short time.

5. Measurement of G . Poynting's Method.

G has been measured by the aid of the "common balance" by (a) von Jolly, (b) Richarz and Krigar-Menzel, and (c) Poynting. Poynting's method will be described here. The balance used (fig. 8) is of the large

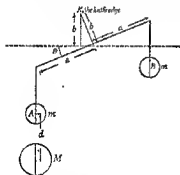


Fig. 8

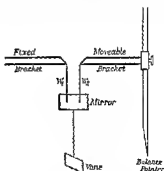


Fig. 9

"bullion balance" type, that is, it is strongly made, with a gun-metal beam and steel knife-edges and planes. From the ends of the beam are suspended equal spherical masses A and B , made of an alloy of lead and antimony. Each has a mass of about 21.6 Kgm. A spherical attracting body M , of mass about 153 Kgm., made of the same alloy, is mounted on a special turntable, so that it can be brought to a point vertically under A , and then under B . In each case the downward attraction is given by $F = G M m / d^2$, and this force tilts the balance beam downwards on the side where the attraction is applied. The tilt is measured in each case by an optical device (see fig. 9) involving

the so-called double suspension mirror of Lord Kelvin. In this arrangement the pointer of the balance is attached to a movable bracket supporting one of two wires, which in turn support a small mirror. The other wire is attached to a fixed bracket. When the balance beam moves, the pointer and one wire W_2 move. Thus the mirror rotates about the stationary wire W_1 . The angular tilt of the balance beam is magnified 150 times by this device. Facing the mirror, and about five metres from it, is a

of this is formed in

telescope, pointing

In this way it is f

moving M from under A to under B , is a little more than one second. This same angle is produced by the addition of a weight of 0.0004 gm. to one end of the balance beam, a fact which is proved by displacing a rider of mass 0.01 gm. a definite distance along the beam and thus increasing its turning moment by a known amount.

The calculation is as follows. Assume that the beam is horizontal when M is removed altogether. Let the length of the beam be $2a$ and let its mid-point be b cm. from the central knife-edge. For equilibrium of the beam in the position shown in fig. 8, when M is under A , the moments of the downward forces on A and B are equal, and

$$(mg + GMm/d^2)(a \cos \theta - b \sin \theta) = mg(a \cos \theta + b \sin \theta),$$

where θ is the angle which the beam makes with the horizontal. A similar equation holds when M is placed under B , and the beam is depressed on the right through θ . Again, when M is removed altogether and a small extra mass m' is attached to A , let the angular tilt once more be θ . Then

$$(mg + m'g)(a \cos \theta - b \sin \theta) = mg(a \cos \theta + b \sin \theta).$$

From these two equations we have

$$GMm/d^2 = m'g \quad . \quad . \quad (17)$$

and

$$G = m'gd^2/Mm. \quad . \quad (18)$$

Corrections have to be applied for (a) the cross attraction of M on the mass which is not above it, (b) the metal removed in making boreholes through A and B to admit the supporting rods, (c) the attraction of M on the balance beam itself. This last correction is made by raising the masses A and B about 25 cm. higher, in another experiment, and finding the attraction of M once more, M being in its former position. Thus the attraction of M on the beam is the same as in the previous case, but the attraction on A and B is altered. Equation (17) now becomes, in the two cases,

$$GMm/d_1^2 + Z = m'g$$

and

$$GMm/d_2^2 + Z = m''g.$$

where Z is the force exerted by M on the beam. By subtraction Z is eliminated, and

$$G = (m'' - m')g/4fm(1/d_2^2 - 1/d_1^2). \quad \dots \quad (19)$$

The change of position of M is found to tilt the floor through an angle of about one-third of a second. This is eliminated by mounting a mass $M/2$ on the turntable at twice the distance of M from the axis and diametrically opposite M . Allowance is made for the attraction of this mass on A and B . The balance is enclosed in a case to reduce air currents and the deposition of dust. The beam is kept free, supported on its knife-edge and therefore under strain, throughout a set of readings, because it cannot be lowered and raised so that the knife-edge again comes into precisely the same line. All moving parts, such as supports for weights and riders, are supported independently of the balance case. Poynting's final results are

$$G = 6.6984 \times 10^{-8} \text{ c.g.s. units,}$$

$$\text{Mean density of the earth} = 5.4934 \text{ gm. per c.c.}$$

The probable errors are not given.

6. Possible Variations in G .

Experiments have been made to test whether the force of gravitational attraction is affected by various changes in conditions. Work by Eötvös and others with the torsion balances revealed no change in G exceeding the limit of experimental error, that is, greater than $10^{-8} G$, when the nature of the attracting masses was varied over a wide range of substances; in other words, G is independent of the nature of the masses. The same researches proved that G is independent of the state of chemical combination of the elements in the masses. The fact that an element is radioactive has also been shown to have no effect on G . Shaw, using a torsion balance in the same manner as Boys, varied the temperature of the large lead masses from 0° to 250° C. , but no change in G exceeding the limit of experimental error could be detected. That is, any variation in G with temperature is less than $2 \times 10^{-6} G$ per degree centigrade. Poynting and Phillips obtained the same negative result, using the balance method. Various experimenters have investigated the gravitational attractions of crystals, that is, of anisotropic bodies. The value of G obtained remains independent of the direction of the crystallographic axes to within $10^{-8} G$, the limit of experimental error. For example, the weight of a crystal does not depend on the orientation of its axes with respect to the vertical. Eötvös and his collaborators, and also Majorana and Austin and Thwing, have investigated the effect of interposing layers of different media between attracting and attracted bodies. Very dense media, such as lead and mercury, were used. No effect could be detected. For example, in one case 5 cm. of lead produced no detectable change; that is, any change produced did not exceed $2 \times 10^{-11} G$.

7. Relativity and the Law of Gravitation.

The discovery of the laws of relativity has profoundly changed the views of physicists on the subjects of mass and gravitation. A detailed exposition must be sought in works on relativity,* but a few special points may be noted here. In discussing these it is advisable to consider the mass of a body from two points of view. The mass is often defined as the quantity of matter in a body. If a body is known to be moving with a certain acceleration, Newton's second law states that it experiences a force equal to the product of the mass and the acceleration. The mass in this sense is often called the "inert" mass. On the other hand, a body placed in a gravitational field of force experiences a force equal to the mass multiplied by the strength of the field at that point. The mass in this sense is called the "heavy" mass. As was mentioned on p 49, the experiments of Eötvös and others have proved that the accelerations of bodies of different materials placed in the same gravitational field of force are the same to within one part in 10^9 . Further, bodies of any "inert" mass, light, medium or heavy, have exactly the same acceleration in the same field of force. If we write "Force on a body = inert mass \times acceleration", and "Force on a body = heavy mass \times field strength", and apply these statements to one and the same body, we see that the forces are equal, and after dividing and rearranging, we have

$$\text{Acceleration} = \text{heavy mass} \times \text{field strength} / \text{inert mass}.$$

Since the acceleration is constant and independent of the nature of the body, in the same field of force, we have

$$\text{Heavy mass/inert mass} = \text{a constant.} \quad \dots (20)$$

With suitable units the constant is equal to unity. Einstein interpreted this well-known result as meaning that the same quality of a body exhibits itself in one set of circumstances as inertia and in another as weight. He deduced that it is impossible to distinguish between the two following states of a system of bodies: (1) a state of accelerated motion in the absence of a gravitational field of force, (2) a state of rest in a field of gravitational force.

One of the consequences of the restricted theory of relativity, which has been confirmed by experiment, is that of the "inertia of energy", that is, whenever the energy of a body is changed in any way the mass of the body also undergoes a change. The two changes are connected by the relation

$$\text{Change of mass in grammes} = \text{change of energy in ergs}/c^2.$$

* For a brief account, see Wilson, *Modern Physics*, Chap. XVIII, XIX (Blackie & Son Ltd., third edition, 1949)

where c is the velocity of light in vacuo, in cm. per sec. This applies to all forms of energy, including electromagnetic radiation, heat, &c. Thus gravitation is linked up with light and other electromagnetic phenomena. Further, the theory shows that the mass m of a body in motion with velocity v cm. per sec. is not the same as its mass m_0 when it is at rest, but

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \dots \dots \dots (21)$$

This expression has been confirmed by experiments with β -particles from radioactive substances and with other fast particles accelerated to high velocities in atomic accelerators.

The point of view of the generalized theory of relativity can only be hinted at here. All matter or energy modifies the properties of space-time in its neighbourhood, producing what is called a field of gravitation. The property of acting upon a body or an electromagnetic wave belongs to space-time modified in this way by the presence of matter or energy. It is not a direct instantaneous action at a distance produced by an attracting body. The cause of the deformation of space-time in the neighbourhood of matter or energy, that is, the cause of gravitation, is still unknown. The generalized theory enables the law of gravitation to be stated in its most general form, in tensor notation, a form in which it contains the laws of conservation of energy, momentum and mass of classical physics as special cases. As is well known, the generalized theory had three important successes:

- (1) It accounted for the displacement of the perihelion position of the planet Mercury.
- (2) It predicted a lateral displacement of rays of light passing through a gravitational field.
- (3) It predicted a spectral shift of solar rays of light.

Recently there has been a tendency to return to pictorial models of gravitational phenomena. A naïve view, many centuries old, was that gravitational force arose from the presence throughout space of swarms of tiny corpuscles which bombarded an isolated body uniformly. In the region between two bodies, however, there was a deficit of corpuscles and consequently the two bodies were thrust together under the excess bombardment on their more remote sides. Such a hypothesis remained an *ad hoc* one until recent developments on *fundamental particles*. Of these, the neutron, although it is uncharged, interacts with matter almost entirely by means of specifically nuclear forces which are not gravitational and hence its consideration has not thrown any light on this particular problem. On the other hand, the neutrino, which is not only neutral but which has zero rest mass, is not dissimilar

from the corpuscles originally postulated to explain gravitation and further consideration of its properties may lead to a genuine advance. Another related pictorial concept which is being developed is the *geon*; this entity results when the deflection of a ray of light by a gravitational centre is such as eventually to rotate the ray through 360° so that it forms a closed circuit around the gravitational centre.

A still more recent development is the discovery of *anti-matter* in the form of *anti-protons* and *anti-neutrons*. Anti-protons have a negative

charge, and *anti-electrons* or *positrons* occurs. Because our local region of the Universe consists almost entirely of ordinary matter, any anti-matter which is created has only an evanescent life, but an interesting problem arises as to whether gravitational repulsion instead of gravitational attraction exists between matter and anti-matter. It has been shown that the electrostatic field of an atom polarizes the vacuum in its neighbourhood to produce virtual electron-positron pairs. The magnitude of this con-

tribution to the gravitational field has been calculated, and gravitational experiments of Eötvös detected no difference between platinum and other materials to $\frac{1}{2}$ part in 10^{-9} . There is therefore no existing evidence for gravitational repulsion.

CHAPTER IV

Elasticity

1. Introduction.

The behaviour of bodies subjected to deforming forces constitutes the study of elasticity. If the body entirely regains its original size and shape, it is said to be *perfectly elastic*; if it entirely retains its altered shape and size, it is said to be *perfectly plastic*. Actual bodies are intermediate in their behaviour, and the same material will behave differently according as it is in the form of a single crystal or a heterogeneous mass of crystals such as constitute, for example, an ordinary metal bar or wire. Elastic strains are due to distortion of the space lattice within a crystal, while plastic deformations and fractures are produced by the development of slip planes. The study of the behaviour of single crystals involves a fair knowledge of crystal structure; it is discussed briefly on p. 84. Attention will be largely confined to isotropic substances in bulk, that is, substances which exhibit under test the same properties in all directions; anisotropic substances require laborious and complicated mathematical treatment.

The change of shape or size (or both) is termed a *strain*; the forces in equilibrium which produce the strain are often loosely termed the stresses. More correctly, the *stress* is defined as follows. Let F be the force acting across a small plane area A at any angle to its surface. Then the normal component of F divided by the area A is termed the *normal stress*; the tangential component of F divided by the area A is termed the *mean tangential stress*. The criteria of a perfectly elastic body are these:

- (a) A given stress always produces the same strain.
- (b) Maintenance of a given stress results in a constant strain.
- (c) Removal of stress results in complete disappearance of strain.

2. Deviations from Hooke's Law.

It was found experimentally by Hooke in 1679 that, over a considerable range, the strain produced is proportional to the stress applied. This relation, which is termed Hooke's law, forms the basis of the theory of elasticity. If the strain is a simple stretching of the material,

the graphical relation between the stress p and the strain (extension) e is called the *stress-strain curve*. $\Delta l = l - l_0$

$p = \frac{F}{A}$

$e = \frac{\Delta l}{l_0}$

elasticity, holds only up to certain limits, termed the *limit of proportionality* and the *elastic limit*. These two points do not in general coincide. In fig. 1(b), the former is represented by the point P . Its definition is comparatively simple and certain, whereas the direct

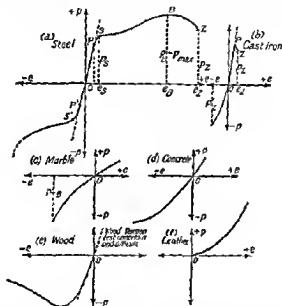


Fig. 1

determination of the elastic limit is a difficult process. Immediately after passing the limit of proportionality the curve shows a marked kink, which after a short interval, about the point S , is followed by a rapid increase of the extension for slowly increasing (and sometimes even for diminishing!) stress. The point S at which the material may be said to flow is called the *yield point*. On further increase of the load, the stress reaches at the point B its greatest value $p_s = p_{max}$, and up to that point the strains extend fairly uniformly over the whole rod.

some point Z , for values p_z and e_z , the rod breaks. The maximum stress and strain p_z and e_z are termed the *breaking stress* and *breaking strain*.

The behaviour of materials under compression is shown by the continuation of the curve below the x -axis. Referring to the p - e curve for steel, we see that a region of proportionality is again initially observed; the point S' , which is the yield-point under compression, is also known as the *crushing limit*; finally a region of flow is obtained, which for ductile materials like steel may extend for a considerable distance without fracture occurring. With brittle metals like cast iron, fracture occurs immediately at the end of the region of proportionality, or after a kink and a short drop in the curve. There is no yield-point and no "necking". Materials like marble, concrete and wood are characterized by no proportionality between stress and strain, even for small stresses, as is shown in figs. 1 (c), (d), (e) and (f). In most cases, when fracture eventually occurs it is produced by the action of shear.

3. Moduli of Elasticity.

The method of measuring a strain varies according to its nature. For simple stretching of a wire, the strain is measured by the increase in length per unit length of the wire.

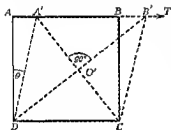


Fig. 2

Now consider a cube of side $ABCD$, fixed at the base and under the action of tangential forces in the direction $AA'BB'$ (fig. 2). The cube takes up the form $A'B'CD$, that is, the volume remains unaltered; such a strain is termed a *shear* and is measured by the angular deformation θ .

Finally, if an isotropic body is uniformly compressed in all directions, it will retain its original shape

but will undergo a volume compression. The strain is measured by the change in volume divided by the original volume.

The ratio of the stress to the strain produced in a body is termed the *elastic modulus*. There are three elastic moduli, according to the nature of the strain, namely:

$$\text{Young's modulus } \rho = \frac{\text{Applied load per unit area of cross-section}}{\text{Increase in length per unit length}}.$$

$$\text{Rigidity modulus } \pi = \frac{\text{Tangential stress per unit area}}{\text{Angular deformation } \theta}.$$

$$\text{Bulk modulus } K = \frac{\text{Compressive (or tensile) force per unit area}}{\text{Change in volume per unit volume}}.$$

It is found experimentally that when a body undergoes a linear tensile strain it experiences a lateral contraction as well. Since this contraction is directly proportional to the extension, a fourth elastic constant termed *Poisson's ratio* and denoted by σ is introduced; this is defined as the decrease in width per unit width divided by the longitudinal strain. The four elastic constants are interdependent, since any change in size and shape of a body may be obtained by first changing the size but not the shape (volume strain) and then changing the shape but not the size by means of a shear.

4. Components of Stress and Strain.

Consider a parallelepiped $ABCDEFGH$ of the material with its sides parallel to the axes of co-ordinates Ox , Oy and Oz as in fig. 3. Then simple considerations of equilibrium show that if no translational or rotational motion is to occur, the most general distribution of forces reduces to three different normal stresses X_x , Y_y , Z_z and three different pairs of tangential stresses $X_y = Y_x$, $Z_x = X_z$, $Y_z = Z_y$. The notation is such that the subscript indicates the axis perpendicular to the face across which the normal or tangential force is acting. The strain may likewise be resolved into six components e_{xx} , e_{yy} , e_{zz} and $e_{yz} = e_{zy}$, $e_{xz} = e_{zx}$, $e_{xy} = e_{yx}$ where the former constitute the strains produced by the normal stresses and the latter the shearing strains. Thus e_{xx} is the relative displacement of planes perpendicular to Oy and Oz respectively and initially at unit distance apart.

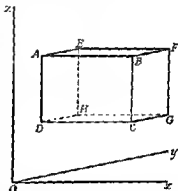


FIG. 3

5. Strain Ellipsoid.

Consider a sphere with radius r and centre O , and let (x, y, z) be the co-ordinates of a point on its surface (fig. 4). Suppose that it is strained into a symmetrical figure with centre O' , that $O'A'$, $O'B'$, $O'C'$ have magnitudes a' , b' , c' and correspond to OA , OB , OC , and that (x', y', z') corresponds to (x, y, z) .

Since the ratio of parallel lines is unaltered by strain, we see by fig. 4 that

$$\frac{x}{r} = \frac{x'}{a'}, \quad \frac{y}{r} = \frac{y'}{b'}, \quad \frac{z}{r} = \frac{z'}{c'}.$$

Now

$$x^2 + y^2 + z^2 = r^2.$$

Hence

$$\frac{x'^2}{a'^2} + \frac{y'^2}{b'^2} + \frac{z'^2}{c'^2} = 1,$$

or (x', y', z') is a point on an ellipsoid with a', b', c' as conjugate diameters. Since there are only three diameters of an ellipsoid which are mutually perpendicular, there are, in general, only three mutually perpendicular diameters of the sphere which remain mutually per-

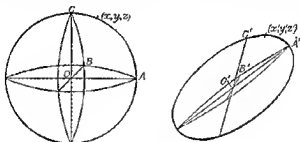


Fig 4

pendicular after straining. These are termed the *axes of strain* and the corresponding strains are termed the *principal strains*.

6. Relations between the Elastic Constants.

Since for isotropic substances the directions of the axes of strain will be those of the normal stresses, the most general stress at a point will be P_1, P_2, P_3 along Ox, Oy, Oz respectively. Hence $X_x = P_1, Y_y = P_2$ and $Z_z = P_3$, while $X_y = Y_x = Z_x = Z_y = 0$. The corresponding strains will be

$$e_{xx} = \frac{1}{q} \{P_1 - \sigma(P_2 + P_3)\},$$

$$e_{yy} = \frac{1}{q} \{P_2 - \sigma(P_3 + P_1)\},$$

$$e_{zz} = \frac{1}{q} \{P_3 - \sigma(P_1 + P_2)\},$$

while $e_{xy} = e_{yz} = e_{zx} = 0$.

Solving for P_1 , P_2 and P_3 , we have

$$\left. \begin{aligned} P_1 &\approx \lambda\delta + 2n'e_{xx} \\ P_2 &\approx \lambda\delta + 2n'e_{yy} \\ P_3 &\approx \lambda\delta + 2n'e_{zz} \end{aligned} \right\} \quad (1)$$

where

$$\delta = e_{xx} + e_{yy} + e_{zz} \quad \lambda = \sigma q / (1 + \sigma)(1 - 2\sigma) \quad \text{and} \quad 2n' = q / (1 + \sigma).$$

The *dilatation* δ measures, to a first order, the fractional change in volume, since it is the sum of the principal extensions

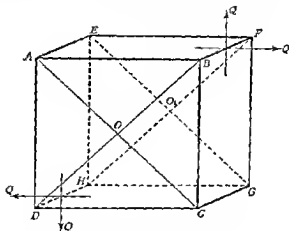


Fig. 5

For a uniform compression or dilatation $P_1 = P_2 = P_3 = P$. Hence, adding equations (1), we have

$$\delta = \frac{3P}{3\lambda + 2n'} \quad \dots \dots \dots (2)$$

Now the bulk modulus K is defined by

$$K = P/\delta.$$

Hence

$$K = \frac{q}{3(1 - 2\sigma)} \quad \dots \dots \dots (3)$$

It remains to identify n' with n , the rigidity modulus. We see from fig. 5 that if a simple stress Q acts on four sides of a cube $ABCDEFGH$, the stresses across the diagonal planes $ACGE$, $BDHF$

will be compressive and extensive respectively and each of magnitude Q . Taking the axes Ox, Oy, Oz as parallel to OB, OA, OO_1 , we have $X_x = Q, Y_y = -Q, Z_z = 0$, with corresponding strains

$$e_{xx} = -e_{yy} = \left(\frac{1+\sigma}{q}\right)Q, e_{zz} = 0.$$

Then

$$\tan DA'O' = \frac{DO'}{A'O'} = \frac{1+e_{xx}}{1+e_{yy}} \frac{DO}{AO} = \frac{1+e_{xx}}{1+e_{yy}},$$

where the dashed letters correspond to the strained cube (see fig. 2). Since the shear strain $\theta = \angle DA'B' - \angle DAB = 2\angle DA'O' = \pi/2$,

$$\tan \frac{\theta}{2} = \frac{\tan DA'O' - 1}{1 + \tan DA'O'} = \frac{e_{xx} - e_{yy}}{2 + e_{xx} + e_{yy}} = \frac{1}{2}(e_{xx} - e_{yy}).$$

For small angles, therefore,

$$\theta = e_{xx} - e_{yy} = 2(1+\sigma)Q/q.$$

Now the modulus of rigidity is defined by

$$n = Q/\theta = q/2(1+\sigma), \quad \dots \dots \dots (4)$$

and, by comparison with equations (1), $n' = n$.

Eliminating σ from (3) and (4), we obtain the important relations

$$\text{or } \left. \begin{aligned} q &= \frac{9nK}{3K+n} \\ \sigma &= \frac{3K-2n}{6K+2n} \end{aligned} \right\} \dots \dots \dots (5)$$

The expression for Poisson's ratio may be written $3K(1-2\sigma) = 2n(1+\sigma)$. Since K and n are both positive, σ cannot be greater than $\frac{1}{2}$ nor less than -1 .

7. Principle of Superposition.

The preceding theory is based on the assumption that the effects produced by the different stresses are quite independent of one another. The applicability of this principle of superposition is confirmed by experiment. In particular, Guest* made a careful study of the behaviour of thin tubes under combined stresses. He showed that various stresses, such as internal compression, tension, and torsion, could be applied simultaneously and combined in different proportions, but that initial yielding occurred only when a specific total shearing stress was attained.

* *Phil. Mag.* (5), Vol. 50, p. 69 (1900).

8. Bending of Beams.

When a beam is bent by an applied couple, the filaments of the beam are compressed in the region nearest the inside of the curve and extended in the region nearest the outside. The filament which experiences no change in length when the curvature is applied is termed the *neutral filament* or *neutral axis*.

Suppose a rod $ABOD$ (fig. 6) is bent into a circle and that the radius of the neutral axis PQ is ρ . Then if we consider a filament $P'Q'$ of the rod, a distance z from PQ , we have

$$P'Q' = (\rho + z)\phi.$$

Hence the extension of the filament is

$$e = P'Q' - PQ = (\rho + z)\phi - \rho\phi = z\phi \quad \dots (6)$$

and the strain, since the original length was $\rho\phi$, is z/ρ . If the area of cross-section is a , the force across the area is $\frac{Ez}{\rho} a$.

The couple due to these forces is thus $\frac{Ez^2}{\rho} az$, and the total couple, or *bending moment*, due to all the filaments in the rod, which must equal the external applied couple G when the rod is in equilibrium, will be

$$G = \frac{E}{\rho} \Sigma az^2. \quad \dots (7)$$

The quantity Σaz^2 is analogous to the moment of inertia about the axis $z=0$ and is termed the *geometrical moment of inertia* of the cross-section about that axis, which is perpendicular to the plane of the paper. If the actual area is A and the radius of gyration is denoted by k ,

$$G = \frac{E A k^2}{\rho}. \quad \dots (8)$$

The quantity $E A k^2$ is sometimes termed the *flexural rigidity*.

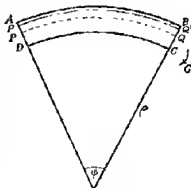


FIG. 6

9. Beams under Distributed Loads.

Consider an element of the rod, of length dx , at a distance x from some origin on the neutral axis, and let the load per unit length be w (fig. 7). Then $w dx$ is the load on dx ; let the shearing forces and the bending moments be $F, G, F + dF, G + dG$ at x and $x + dx$ respectively. Then

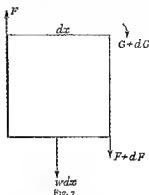
$$\frac{dF}{dx} = -w \quad . \quad . \quad . \quad (9)$$

and

$$\frac{dG}{dx} = -F, \quad . \quad . \quad . \quad (10)$$

or

$$\frac{d^2G}{dx^2} = w. \quad . \quad . \quad . \quad (11)$$



10. Relation between Bending Moment and Deflection.

If ρ is the radius of curvature of the beam at a point where the depression is y (fig. 8), we have

$$\pm \frac{1}{\rho} = \frac{d^2y/dx^2}{\left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2}}$$

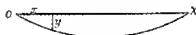


Fig. 8

Since $\left(\frac{dy}{dx}\right)^2 \ll 1$, it is approximately true that

$$\frac{1}{\rho} = \pm \frac{d^2y}{dx^2}$$

Hence, from (8), $G = qAk^2 \frac{d^2y}{dx^2} \quad . \quad . \quad . \quad (12)$

Combining equations (10), (11) and (12), we have

$$qAk^2 \frac{d^4y}{dx^4} = w \quad . \quad . \quad . \quad (13)$$

and

$$qAk^2 \frac{d^3y}{dx^3} = -F. \quad . \quad . \quad . \quad (14)$$

11. Solutions of Beam Problems.

The four constants of integration required for the solution of (13) are determined by the end conditions of the beam. Three cases usually occur:

(1) *Free end with no load.*

$$F = 0, \text{ hence } \frac{d^3y}{dx^3} = 0,$$

and

$$G = 0, \frac{d^2y}{dx^2} = 0.$$

If a load W is attached to the free end, $F = W$.

(2) *End supported but not gripped.*

$$G = 0, \text{ hence } \frac{d^2y}{dx^2} = 0, \text{ and } y \text{ is known.}$$

(3) *End clamped.*

$\frac{dy}{dx}$ is known and usually equal to zero, and y is known.

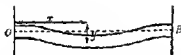


Fig. 9

In the solution of beam problems care must be taken that the boundary conditions inserted after integration apply to that portion only of the beam within whose limits the differential equation was originally formulated. It is often convenient to divide the problem into two or more parts at some convenient point such as a support, as illustrated in the solution of Ex. 4, p. 314, and then to equate elevations and slopes at the junction.

EXAMPLE — *Uniform beam clamped horizontally at both ends under a uniformly distributed load (fig. 9).*

This example of the application of equations (12), (13) and (14) will now be worked out; other examples for the reader will be found on p. 315.

Writing D for d/dx , D^2 for d^2/dx^2 , &c., and using (13), we have

$$q d^2 D^4 y = w.$$

Integrating four times, we have

$$qAk^2D^2y = wx + A, \quad \dots \dots \dots (15)$$

$$qAk^2D^2y = \frac{wx^2}{2} + Ax + B, \quad \dots \dots \dots (16)$$

$$qAk^2Dy = \frac{wx^3}{6} + \frac{Ax^2}{2} + Bx + C, \quad \dots \dots \dots (17)$$

$$qAk^2y = \frac{wx^4}{24} + \frac{Ax^3}{6} + \frac{Bx^2}{2} + Cx + H. \quad \dots \dots \dots (18)$$

From case (3) above, the end conditions are

$$Dy = y = 0 \text{ for } x = 0, \quad Dy = y = 0 \text{ for } x = l,$$

where l is the length of the beam.

Hence, from (17) and (18), $C = H = 0$,

$$\frac{1}{2}Bl^2 + \frac{1}{6}Al^3 + \frac{1}{24}wl^4 = 0,$$

$$Bl + \frac{1}{2}Al^2 + \frac{1}{6}wl^3 = 0.$$

Solving for A and B , we obtain

$$A = -\frac{1}{2}wl,$$

$$B = -\frac{1}{12}wl^2.$$

The complete solution is therefore

$$\begin{aligned} qAk^2y &= \frac{1}{24}wx^4 - \frac{1}{12}wlx^3 + \frac{1}{24}wl^2x^2 \\ &= \frac{1}{24}wx^2(x^2 - 2lx + l^2) = \frac{1}{24}wx^2(x - l)^2. \quad \dots \dots (19) \end{aligned}$$

Further,

$$\begin{aligned} \theta &= qAk^2Dy \\ &= \frac{w}{12}(0x^2 - 6lx + l^2), \quad \dots \dots \dots (20) \end{aligned}$$

and

$$\begin{aligned} F &= -qAk^2D^2y \\ &= w(l - x). \quad \dots \dots \dots (21) \end{aligned}$$

By (20), the bending moment is zero when

$$6x^2 - 6lx + l^2 = 0,$$

and the maximum deflection occurs at the centre of the beam and is given by

$$y = \frac{wl^4}{384qAk^2}.$$

12. Thin Rods under Tension or Thrust: Euler's Theory of Struts.

It can be shown that the bending moment is always equal to qAk^2/ρ , even if a tension or thrust is present in addition to the bending couple.

Let a thrust P act at the ends of a thin rod of length l (fig. 10).

As P is increased there occurs a critical value at which the rod will buckle, unless it is constrained, when it will ultimately fail by crushing.

To find the critical value of P , let the rod be initially slightly bent and consider any point S on the rod with co-ordinates (x, y) . If G is the bending moment, and we take moments about S , we have

$$G = -Py. \quad \dots \dots (22)$$

But

$$G = qAl^2 D^2 y.$$

Hence

$$qAl^2 D^2 y = -Py$$

If we write this in the form $D^2 y = -m^2 y$, where $m^2 = P/qAl^2$, the solution is

$$y = A \cos mx + B \sin mx.$$

Substituting for the boundary conditions

$$y = 0 \text{ when } x = 0, \quad y = 0 \text{ when } x = l,$$

we have

$$A = 0, \text{ and } B \sin ml = 0$$

The latter condition is satisfied if $B = 0$, when the rod is straight, or for $\sin ml = 0$, when $ml = \pi, 2\pi, 3\pi$, &c.

The first stable bending position therefore occurs when $m = \pi/l$ the force is then

$$P = qAl^2 \pi^2 / l^2 \quad \dots \dots (23)$$

and

$$y = B \sin \pi x / l. \quad \dots \dots (24)$$

Since at the centre of the rod $x = l/2$, from (24), $B = y_{\max}$. The rod may therefore bend to any extent within certain limits, provided P reaches the critical value given by (23). In the calculation the curvature has been put equal to $D^2 y$, and this approximation gives the value of the limits of bending.

When $m = 2\pi/l$, equilibrium is again obtained: the various positions clearly correspond to multiples of half a sine-wave.

Euler's theory is only in approximate agreement with experiment; Southwell has given a more satisfactory but much more complicated treatment.

13. Uniform Vertical Rod Clamped at Lower End. Distributed Load.

The problem of a uniform vertical rod under a distributed load and clamped at its lower end has many important applications. Thus



e.g. there is a limit to the height to which a tree can grow before it bends under its own weight. In fig. 11 consider two points Q and Q' , with co-ordinates (x, y) and (x', y') , on the bending rod OB . The weight per unit length w is generally a function of x ; let the weight of an element of length at Q' be $w dx'$.

The moment of this element about Q will be $w dx'(y' - y)$, and the total bending moment about Q , due to the length above Q , is

$$G = \int_l^x w(y - y') dx',$$

where l is the length of the rod.

Differentiating both sides with respect to the upper limit x , we have

$$\begin{aligned} \frac{dG}{dx} &= \int_l^x w \frac{dy}{dx} dx' + [w(y - y')]_{x'=x} \\ &= \frac{dy}{dx} \int_l^x w dx'. \end{aligned}$$

Now the total load above Q is $-\int_l^x w dx' = W$, say. Hence

$$\frac{dG}{dx} = -W \frac{dy}{dx}$$

or

$$qAk^2 \frac{d^2 y}{dx^2} = -W \frac{dy}{dx} \quad \dots \dots (25)$$

The solution of (25) depends on the nature of W and may be very complicated. For the special case of a uniform distribution of load, $W = w(l - x)$. Then

$$qAk^2 \frac{d^2 p}{dx^2} = -w(l - x)p \quad \dots \dots (26)$$

or

$$\frac{d^2 p}{dx^2} = -\beta(l - x)p,$$

where

$$p = \frac{dy}{dx} \text{ and } \beta = w/qAk^2.$$

Finally, putting $l - x = z$, we have, since $\frac{d^2 p}{dx^2} = \frac{d^2 p}{dz^2}$,

$$\frac{d^2 p}{dz^2} = -\beta zp. \quad \dots \dots (27)$$

To solve equation (27) we express p in terms of a power series

$$p = \alpha_0 + \alpha_1 x + \alpha_2 x^2 + \alpha_3 x^3 + \dots \quad (28)$$

$$\frac{d^2 p}{dx^2} = 2\alpha_2 + 2.3\alpha_3 x + 3.4\alpha_4 x^2 + \dots \quad (29)$$

Hence, combining equations (27), (28) and (29), and equating coefficients of powers of x , we obtain

$$2\alpha_2 = 0, \quad 2.3.\alpha_3 = -\beta\alpha_0, \quad \text{&c.}$$

Hence

$$p = \alpha_0 \left(1 - \frac{\beta x^3}{2.3} + \frac{\beta^2 x^6}{2.3.5.6} - \dots \right) \\ + \alpha_1 \left(x - \frac{\beta x^4}{3.4} + \frac{\beta^2 x^7}{3.4.6.7} - \dots \right)$$

The constants α_0, α_1 are determined from the boundary conditions,

$$p = 0 \text{ when } x = l, \quad \frac{dp}{dx} = 0 \text{ when } x = 0$$

Hence $\alpha_1 = 0$ and

$$0 = 1 - \frac{\beta l^3}{6} + \frac{\beta^2 l^6}{180} - \dots \quad (30)$$

If ρ is the density, then $w = g\rho A$, and the maximum height is given by

$$l = 1.90 \left(\frac{q^2}{g\rho} \right)^{\frac{1}{3}} \quad (31)$$

If $\rho = 0.8$ and $g = 10^{31}$ dynes/sq. cm. for deal, the maximum height of a pine tree 15 cm. across is about 27 metres

14. Torsion of Rods.

Consider an element of a circular rod, of area a and at a distance r from the axis of symmetry OO' of the rod (fig. 12). Let the rod be fixed at its lower end at a distance l from a and let a be twisted through an angle ϕ by an external couple. Then if the tangential stress across a is F , the element of couple about the axis which this contributes is

$$dQ = Far$$

Now if the angle of shear is θ ,

$$r\phi = l\theta$$

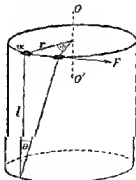


Fig. 12

Also, since $n = F/\theta$, where n is the rigidity modulus,

$$dQ = \frac{n\phi}{l} \alpha r^2.$$

Hence the total couple about the axis is

$$Q = \frac{n\phi}{l} \Sigma \alpha r^2.$$

Since the rod has a circular cross-section, $\Sigma \alpha r^2$ is the geometrical moment of inertia of the section of the rod about the axis. Since

$$\Sigma \alpha r^2 = \int_0^R 2\pi r dr \cdot r^2 = \frac{1}{2} \pi R^4 = Ak^2,$$

$$Q = \frac{1}{2} \frac{\pi n \phi R^4}{l}, \quad \dots \dots \dots (32)$$

where R is the radius of the rod. The quantity Ql/ϕ is sometimes termed the *torsional rigidity*.

For rods of any other cross-section $Ql/n\phi$ is less than Ak^2 . The solutions for elliptic, equilaterally triangular and square sections were given by St. Venant, who showed that the torsion involves a longitudinal displacement in the cross-section. The treatment of St. Venant is based on a general principle enunciated by him, that the strains which are produced in a body by the application, to a small part of its surface, of a system of forces statically equivalent to zero force and zero couple are of negligible magnitude at distances which are large compared with the linear dimensions of the part.

It is only with cross-sections of a high degree of symmetry, however, that mathematical expressions can be obtained for $Ql/n\phi$. Recourse must otherwise be made to analogous equations in other branches of physics, which are more susceptible to investigation. Thus Prandtl pointed out that the deviation from a plane of the surface of a soap film which covers a hole of the same size as the cross-section of the bar, and which has an excess pressure on one side, may be used to obtain the form of the function determining $Ql/n\phi$. The values for $Ql/n\phi$ and for the geometrical moments of inertia of different sections about the axis are given below.

Circular area, radius R .

$$Ql/n\phi = \frac{1}{2} \pi R^4; \quad Ak^2 = \frac{1}{2} \pi R^4.$$

Elliptical area, semi-axes a and b .

$$Ql/n\phi = \frac{\pi a^3 b^3}{a^2 + b^2}; \quad Ak^2 = \frac{1}{4} \pi ab(a^2 + b^2).$$

Rectangular area, sides $2a$ and $2b$,

$$Ql/n\phi = \frac{16ab^3}{3} - b^4 \left(\frac{4}{\pi} \right)^2 \left\{ \sum_{m=0}^{\infty} \frac{1}{(2m+1)^3} \tanh \frac{(2m+1)\pi a}{2b} \right\},$$

where m has the values $0, 1, 2, 3, \dots$:

$$Ak^2 = \frac{4}{3}ab(a^2 + b^2)$$

For a square, this gives

$$Ql/n\phi = 2.2492a^4, \quad Ak^2 = 8a^4/3 = 2.667a^4.$$

If $a = 3b$, the sum of the infinite series of hyperbolic tangents differs by less than 1 part in 5000 from 1.0015.

For a flat strip, therefore,

$$Ql/n\phi = ab^3 \left(\frac{16}{3} - 3.361b/a \right).$$

Hence for circular, elliptic, and rectangular strips of the same cross-sectional area and length, the relative torsional rigidities are in the ratio $1 : 2b/a : 2\pi b/3a$.

Rectangular suspensions have the double advantage of small torsional rigidity combined with large surface area for radiation of heat and are therefore often used in the construction of galvanometers.

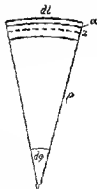


Fig. 13

15. Energy in a Strained Body.

(a) A bent beam.

Consider a short length dl of a filament of a bent beam (fig. 13). Let the cross-section of the filament be a and let it be situated at a distance r from the neutral axis. Then if we use the results of section 8, p. 58, the work done in stretching this filament by an amount e will be

$$\text{Force} \times \text{Distance} = \text{Stress} \times \text{Area} \times \text{Distance}$$

$$= \text{Elastic Modulus} \times \text{Strain} \times \text{Area} \times \text{Distance}$$

$$= \int_0^e q a \frac{e}{dl} de = \frac{1}{2} q a r^2 \frac{dl}{\rho^2}.$$

Hence the total energy of the whole cross-section A of the rod of length dl is

$$\begin{aligned} dV &= \frac{1}{2} \frac{q}{\rho^2} dl \sum \alpha x^2 \\ &= \frac{dl}{2\rho^2} q A k^2. \end{aligned}$$

But

$$G = \frac{q A k^2}{\rho}.$$

Hence the energy of the whole rod is

$$V = \int_0^l \frac{G^2}{2q A k^2} dl. \quad \dots \dots \dots (33)$$

(b) *A rod of circular cross-section under torsion.*

If the couple applied to a rod under torsion is Q , the work done in twisting the rod through an angle $d\phi$ is

$$dV = Q d\phi.$$

Now from equation (32)

$$Q = \frac{\pi n \phi R^4}{2l}.$$

Hence

$$V = \frac{\pi n R^4}{2l} \int_0^{\phi_0} \phi d\phi = \frac{1}{2} Q_0 \phi_0 = \frac{Q_0^2 l}{n \pi R^4},$$

or, alternatively,

$$V = \int \frac{Q^2}{n \pi R^4} dl, \quad \dots \dots \dots (34)$$

where dl is measured along the rod.

16. Spiral Springs.

Let the coils of a spiral spring (fig. 14) be inclined at an angle α to the horizontal plane when the spring is stretched by a force W . We consider any point A on the coils; if a is the radius of the cylinder on which the coils are wound, the external couple at A is Wa . This couple results in a torsional shear $F = W \cos \alpha$ in the tangent plane to the coils at A and a tension $T = W \sin \alpha$ along the tangent to the coils.

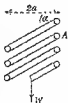


Fig. 14

The couple across the section at A can be resolved into a torque $Q = Wa \cos \alpha$ acting in the plane of the section and a bending moment $G = Wa \sin \alpha$ with its axis perpendicular to the section at A .

Then if x is the final extension of the spring, the work done in stretching is $V = \int_0^x W dx$, where W is now the final stretching force and is equal to the suspended weight Mg if the extension is produced in that way. V must be equal to the sum of equations (33) and (34). Hence

$$V = \frac{1}{2} \int_0^x \frac{G^2}{gAk^3} dl + \int_0^x \frac{Q^2}{\pi nR^4} dl,$$

or

$$\int_0^x W dx = \frac{1}{2} \frac{G^2}{gAk^3} + \frac{Q^2 l}{\pi nR^4}.$$

Derive
Eqn.

Substituting for G and Q , we have

$$\int_0^x W dx = \frac{1}{2} \frac{W^2 a^2 \sin^2 \alpha}{gAk^3} + \frac{W^2 a^2 \cos^2 \alpha}{\pi nR^4}.$$

Differentiating both sides with respect to x , we have

$$\frac{dx}{dW} = a^2 \left(\frac{\sin^2 \alpha}{gAk^3} + \frac{2 \cos^2 \alpha}{\pi nR^4} \right).$$

Since $W = 0$ when $x = 0$,

$$x = W a^2 \left(\frac{\sin^2 \alpha}{gAk^3} + \frac{2 \cos^2 \alpha}{\pi nR^4} \right) \quad \dots (35)$$

If α is small, this becomes approximately

$$x = \frac{2 W a^2}{\pi nR^4} \quad \dots (36)$$

Substituting the value $k^3 = \frac{1}{2} \pi R^3$ for a wire of circular section in (35), we obtain

$$x = \frac{2 W a^2}{\pi R^4} \left(\frac{2 \sin^2 \alpha}{g} + \frac{\cos^2 \alpha}{n} \right) \quad \dots (37)$$

In addition to the vertical motion of the free end, there is an angular displacement in the horizontal plane. If the end of the wire is twisted through ϕ , the torsion gives rise to a horizontal angular displacement $\beta = \phi \sin \alpha$. Since

$$Q = W \cos \alpha = \frac{\pi n R^4 \phi}{2l},$$

$$\beta = \frac{2 W a l \sin \alpha \cos \alpha}{\pi n R^4}; \quad \dots (38)$$

this will cause the spring to coil up, since it acts inwards.

On the other hand, the bending moment produces a horizontal angular rotation of the free end amounting to

$$\int_0^l \frac{dl \cos \alpha}{\rho} = \frac{W a \sin \alpha \cos \alpha}{q A k^2} \int_0^l dl = \frac{4 W a l \sin \alpha \cos \alpha}{q \pi R^4}, \quad \checkmark$$

and this causes the spring to uncoil, since it acts outwards.

The total angular displacement as the spring coils up is therefore

$$\frac{2 W a l \sin \alpha \cos \alpha}{\pi R^4} \left(\frac{1}{n} - \frac{2}{q} \right), \quad \checkmark \quad \dots \quad (39)$$

and is greatest when $\alpha = 45^\circ$.

The spring will coil or uncoil according as $\frac{1}{n} \gtrless \frac{2}{q}$. Since for most metals $q > 2n$, spiral springs of circular section generally coil up when stretched. For a spring made of flat strip of rectangular section of sides $2a$ and $2b$, the total angular displacement is

$$\frac{3 W R l \sin \alpha \cos \alpha}{16 a b^3} \left\{ \frac{1}{n(1 - 3.361 \times 3b/16a)} - \frac{4}{q} \right\}. \quad (39a)$$

17. Vibrations of Stretched Bodies.

The general treatment of the vibrations of stretched bodies is beyond the scope of this book. A few simple cases, however, are of considerable importance.

(a) Transverse vibrations of a loaded bar.

Consider a light rod projecting horizontally from a clamped end, with the free end carrying a weight W .

If the restoring force is F when the deflection is y_1 ,

$$F = -W d^2 y_1 / d\zeta^2.$$

Further, from Ex. 3, p. 313, $q A k^2 y_1 = \frac{F l^3}{3}$.

Hence $\frac{d^2 y_1}{d\zeta^2} = -m^2 y_1$, $\dots \dots \dots (40)$

where $m^2 = 3q A k^2 / (W l^3)$. The solution of (40) gives

$$t = \frac{2\pi}{m} = 2\pi \sqrt{\frac{W l^3}{3q A k^2}} \quad \dots \dots \dots (41)$$

✓ (b) Vertical oscillations of a loaded spring.

In the case of a flat spring, only the torsional energy comes into account. The potential energy when the spring is subjected to a couple

Wa has been shown to be $V = W^2 a^2 / (\pi n R^4)$. But from (36), the vertical extension is $x = 2W a^2 / (\pi n R^4)$.

Hence
$$V = \frac{\pi n R^4}{4la^2} x^2. \quad (42)$$

Let the velocity of the moving mass be dx/dt at the instant when the extension is x . Then the kinetic energy of the mass is $\frac{1}{2}W(dx/dt)^2$. The kinetic energy of the spring itself must also be taken into consideration. If the extremity of the wire moves with a velocity dx/dt , the kinetic energy of an element ds of the wire a distance s from the fixed end will be $\frac{1}{2}m \left(s \frac{dx}{l dt} \right)^2 ds$, where m is the mass per unit length of the spring and l is its total length. The total kinetic energy associated with the spring is therefore

$$\int_0^l \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 \frac{s^2}{l^2} ds = \frac{1}{6} w \left(\frac{dx}{dt} \right)^2, \quad \checkmark$$

where w is the mass of the whole spring. The total kinetic energy of the system is therefore

$$\frac{1}{2} (W + w/3) \left(\frac{dx}{dt} \right)^2. \quad \checkmark$$

Since the sum of the potential and kinetic energies of the whole system is constant,

$$\frac{1}{2} (W + w/3) \left(\frac{dx}{dt} \right)^2 + \frac{\pi n R^4}{4la^2} x^2 = \text{const.}$$

An additional term $(W + w/3)x$ representing the change in potential energy under gravitational forces should be included for vertical motion, but it makes no difference to the period of oscillation, which would be unaltered if g were ineffective as in horizontal oscillations.

Differentiating with respect to t , we have

$$(W + w/3) \frac{d^2x}{dt^2} + \frac{\pi n R^4}{2la^2} x = 0$$

This is of the form $\frac{d^2x}{dt^2} = -m^2x$, where

$$m^2 = \frac{\pi n R^4 / 2la^2}{W + w/3}.$$

The period is $t = 2\pi/m = 2\pi \sqrt{\frac{W + w/3}{\pi n R^4 / 2la^2}}. \quad (43)$

18. Experimental Determination of the Elastic Constants.

Methods for measuring η and α will now be described; the measurement of K is described in the chapter on compressibility (p. 90).

Extension may be measured in the following ways: (1) by a micrometer screw, (2) by an indicating dial, (3) by a microscope, (4) by a

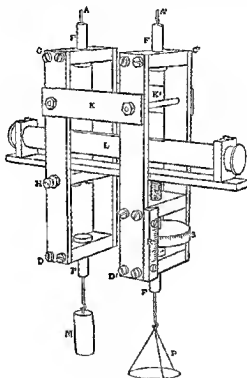


Fig. 15

(From Seale, *Experimental Elasticity* (Camb. Univ. Press))

multiplying lever (mechanical magnification), (5) by optical magnification, (6) by optical interference, (7) by change in electrical resistance (e.g. Bridgman's work, Chapter V, p. 91), (8) by Whiddington's method* of observing the alteration of pitch of a heterodyne beat note, produced by the change in capacity of a condenser when the distance between the plates is varied.

* Whiddington, *Phil. Mag.*, Vol. 40, p. 634 (1920).

19. Young's Modulus.

(a) *Scarle's statical method.*

The apparatus consists of a framework $CC'DD$ (fig. 15), which is supported by two vertical wires A, A' fastened to clamps at P (K and K' being loosely pivoted). Inside the framework rests a spirit-level L supported by the horizontal bar H and the end of a thick screw S . A large graduated drum-head is attached to S and moves over a vertical scale R , as shown. From one side of the framework is suspended a heavy constant weight M and from the other a heavy scale-pan P . In using the apparatus the spirit-level is first adjusted to the horizontal position by turning the drum-head on S . A known load is then placed in P and the distance through which S has to be turned in order to bring the level back to a horizontal position is noted. Further loads are then added and the process is repeated until a given maximum is reached. Readings are then taken with decreasing load.

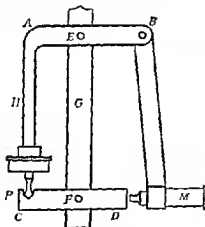


Fig. 16

Since Young's modulus is defined by stress/strain and in this case stress equals load per unit area of cross-section of the wire and strain equals increase in length per unit length, the diameter and length of the wire have still to be determined. The diameter is measured in

original length, and l its extension under the load W ; the value of l/W is determined from the slope of the load-extension diagram

(b) *Ewing's extensometer.*

The preceding method is suitable only for wires; an extensometer such as Ewing's may be used for thicker specimens (fig. 16).

Two horizontal arms AB and CD are pivoted at E and F by screws which pass through the specimen G . The arm BA is bent round to form the vertical rod H , which carries at its lower end a point P ; the point rests in a V-shaped slot cut in the arm CD . Between H and P there is a fine screw-head which may be used to adjust the position of P and to calibrate the instrument. From B is suspended the microscope M , which carries a micrometer scale in the eyepiece and which is focussed on a fine horizontal scratch on the end of CD . When a load is applied to G , P acts as a fulcrum and the extension of the rod is given by FP/DP times the displacement observed in the microscope. Extensions as small as $1/60,000$ of an inch may be measured.

(c) *Bending of a beam.*

The most convenient experimental arrangement is with the load in the middle of the beam and the ends free but supported by knife-edges. Then by a simple extension of Ex. 3, p. 313, the depression is given by

$$y_2 = \frac{W}{2} \frac{1}{3} \left(\frac{l}{2} \right)^3 \frac{1}{qAk^3}$$

The depression may be measured by any one of the eight methods already enumerated. König introduced the use of two mirrors fixed vertically at either of the free ends of the bar, together with a telescope and scale. Then if d is the total change in the scale reading when a load W is applied, s the distance between the mirrors, and ϕ the distance between the scale and the first mirror, it can be shown by simple geometry that

$$d = (2s + 4s)\phi,$$

where ϕ is the actual angle of twist of either of the mirrors.

But by Ex. 3, p. 313,

$$\phi = Dy = \frac{W}{2} \frac{1}{qAk^3} \left(\frac{l}{2} \right)^3 = \frac{x^3}{2}.$$

Hence

$$\phi = \frac{W}{2} \frac{1}{qAk^3} \frac{l^3}{8}$$

so that

$$q = \frac{W}{2} \frac{l^3}{8Ak^3} \frac{(2s + 4s)}{d}.$$

(d) *By angular oscillations of a loaded spring.*

This method is a direct application of the solution of Ex. 9, p. 313

(e) *By transverse vibrations of a rod.*

It may be shown,* by using an analysis somewhat more complicated than that of section 17, p. 71, that for a rod of circular cross-section fixed, for example, in a lathe-chuck and allowed to execute transverse vibrations, the frequency of oscillation is given by

$$n = \frac{m^2 r}{4\pi l^2} \sqrt{\frac{q}{\rho}},$$

* G. F. C. Searle, *Experimental Physics*, pp. 54-6 (Camb. Univ. Press, 1934).

where q is Young's modulus, l length of rod, ρ density of material of rod, r radius of rod, and m is given by $\cosh m \cos m = -1$. The frequency may be determined by resonance with a tuning-fork, and since the remaining quantities are easily found, a value for q is obtained.

20. Measurement of the Rigidity Modulus.

(a) Barton's statical method.

This method is a direct application of formula (32),

$$Q = \frac{1}{2} \frac{\pi n \phi R^2}{l}.$$

The specimen AB hangs vertically (fig. 17), being clamped at A and having a brass cylinder attached firmly to it at B by means of a set-screw. The torque is supplied by weights W carried in small scale-pans, and is made effective by cords acting tangentially to the brass cylinder. The twist between two points a distance l apart on the specimen is obtained by fixing two mirrors M_1 and M_2 to the points by means of set-screws and using the neon lamp and scale method. If c is the radius of the brass cylinder,

$$2Wag = \frac{1}{2} \frac{\pi n q R^2}{l},$$

so that when $2R$ has been determined for several positions on the specimen a may be found

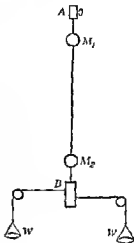


Fig. 17

(b) Vertical oscillations of a loaded spring.

This method is a direct application of equation (43), p. 72.

21. Searle's Method for π and q .

Two equal brass bars A and C of square section are joined by the wire W as shown in fig. 18. The system is suspended by two parallel torsionless threads. If the ends P and P' are made to approach one another symmetrically and are then liberated, the bars will vibrate in a horizontal plane. The centres of the bars O and O' remain approximately at rest, so the action of the wire on the bar and vice versa is given by

vertical axis through its centre, we have

$$I \frac{d^2\theta}{dt^2} = - \frac{qAk^2}{\rho} = - \frac{2gAk^2}{l}$$

This is of the form $\frac{d^2\theta}{dt^2} = -m^2\theta$, where

$$m^2 = \frac{2gAk^2}{Il}$$

and hence the time of oscillation is

$$t_1 = 2\pi \sqrt{\frac{H}{2gAk^2}},$$

where

$$Ak^2 = \frac{\pi R^4}{4}, \quad \dots \dots \dots (44)$$

To determine n for the same wire, the suspensions are removed, and one of the bars is fixed horizontally while the other is suspended from the now vertical

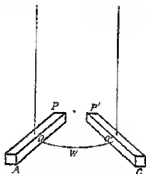


Fig. 18

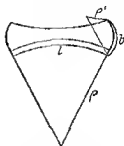


Fig. 19

wire. If the suspended bar is twisted through an angle ϕ and allowed to oscillate, the equation of motion is

$$I \frac{d^2\phi}{dt^2} = -\frac{\pi n R^4}{2l} \phi,$$

which is of the form

$$d^2\phi/dt^2 = -n^2\phi,$$

where $n^2 = \frac{\pi n R^4}{2Il}$, and hence the time of oscillation is

$$t_2 = 2\pi \sqrt{\frac{I}{\frac{1}{2}\pi n R^4/l}}. \quad \dots \dots \dots (45)$$

The ratio q/n is therefore given by t_2^2/t_1^2 , and for the determination of this the values of R , l and I are not required. Moreover, since $q/n = 2(1 + \alpha)$, Poisson's ratio may be directly determined from t_2^2/t_1^2 , without need of other physical measurements.

22. Determination of Poisson's Ratio.

(a) Direct method.

The lateral strain is measured directly with a micrometer screw gauge, while the longitudinal extension is determined by Searle's method or with an extensometer.

(b) Bar method.

When a flat bar of rectangular cross-section is bent by an applied couple, besides the curvature in the plane of the paper (see fig. 19),

there is an anticlastic curvature of radius ρ' in the plane perpendicular to this. It has been shown that the longitudinal strain ϵ at any distance z from the neutral axis is

a

11

ing pointers to the rod and observing the distances and angles traversed when a given couple is applied.

(c) *Use of thin tubes as in bulk modulus determination.* See Chapter V, § 3, p. 88, where $\delta v/v_1 = P(1 - 2\sigma)/g$.

23. Optical Interference Methods for Elastic Constants.

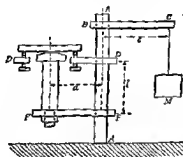


Fig. 20

(From Searle, *Illustrations Experiments* (Camb. Univ. Press).)

examples of various experimental arrangements which have been used are given below.

(a) *Young's modulus by Searle's method*

As fig. 20 shows, DF is a portion of a circular vertical rod AD under test. Two arms DD' and FF' carry an optically flat glass plate and a lens to give Newton's

$$q = \frac{2Mgl(4as - r^2)}{N\pi\lambda r^3},$$

where r is the radius of the rod, a the distance of the centre of the lens from the axis of the rod, and λ the wave-length of the light used to produce the interference pattern.

(b) *Rigidity modulus by Searle's method.*

The apparatus (figs. 21 (a) and (b)) consists of the horizontal rod PQ under test, carrying clamped cross-pieces AB and DE at either end. The piece AB is pierced by a horizontal axis, so that the bar is free to turn and will consequently experience no bending moment when weights M are applied to either D or E . An ivory point C resting on a plane surface S supports the end Q of the bar and also serves as a fulcrum about which the torsion couple arising from the weight M acts. A glass test-plate rests on the centre of the bar.

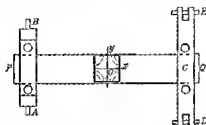


Fig. 21 a

(From Searle, *Miscellaneous Experiments* (Camb. Univ. Press))

Under the action of the couple, the central plane of the bar takes the form of a helicoid surface, the section of which by the horizontal plane gives rise to hyperbolic fringes, as shown in the figure. It may be proved that if $\tau = \frac{1}{2}(\tau_1 + \tau_2)$, where $\tau_1 = \lambda(n-1)/(u_1^2 - v_1^2)$ and $\tau_2 = \lambda(n-1)/(u_2^2 - v_2^2)$, and u and v are the distances from the centre O to fringes measured along directions at 45° and -45° to the x - and y -axes,

$$n = \frac{Mgl}{\pi ab^2 \left(\frac{1}{2} - 3.3616/a \right)},$$

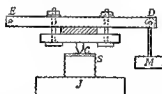


Fig. 21 b

(From Searle, *Miscellaneous Experiments* (Camb. Univ. Press))

where n is the coefficient of torsional rigidity, Mg the applied load, $2l$ the distance DE , and $2a$, $2b$ the width and thickness of the bar respectively.

(c) *Poisson's ratio.*(1) *Cornu's method.*

The method is applicable only to a good reflector, such as glass or a metal which will take a high polish.

A rectangular bar of the material is taken and a plane optical test-plate is placed in contact with it. The bar is then loaded symmetrically as shown in fig. 22; the system of interference fringes produced between bar and test-plate is then

observed. The fringes are hyperbolae (fig. 23), and it may be shown that if the asymptotes make an angle α with the x -axis, $\alpha = \rho/\rho' = \cot^2 \alpha$. The angle may be measured directly with a goniometer eye-piece. Alternatively, if p_1, p_n, q_1, q_n are the distances of the first and n th fringes from the origin O

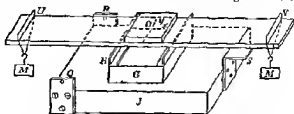


Fig. 22

(From Searle, *Miscellaneous Experiments* (Carb. Univ. Press))

measured along OX and OY respectively, the radii of curvature of the bar in these two directions are given by

$$\rho = \frac{(p_n^2 - p_1^2)}{\lambda(n-1)}$$

and

$$\rho' = \frac{(q_n^2 - q_1^2)}{\lambda(n-1)},$$

whence

$$\alpha = \rho/\rho' = \frac{(p_n^2 - p_1^2)}{(q_n^2 - q_1^2)}.$$

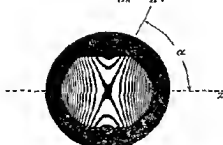


Fig. 23

(From *Handbuch der Physik*, Springer, Berlin)

The method is capable of many variations. For example, the optical test plate may be replaced by a lens, giving Newton's rings. On bending the rod the rings will become increasingly elliptical in shape; finally, when the radius of curvature of the rod in one direction equals that of the lens, rectangular fringes will be obtained.

(2) Method of diffraction haloes

When lycopodium is dusted on a plane polished surface and illuminated by a small source placed in front of the surface, the illuminated particle and its image

send secondary wavelets to the eye and the small source appears surrounded by a diffraction halo. If the surface is bent, the normal will rotate, the angle at which the light enters the eye will change, and the halo will appear deformed. In the experiment of Andrews* (fig. 24) a uniform rectangular brass plate P , one surface of which is polished and dusted with lycopodium, is bent by applied couples and placed a few feet from a small light source L_1 . An observer at E measures the diameter of the elliptical haloes upon the superposed image of the screen S which is seen by reflection in the plate-glass plate G . The lengths of the major and minor axes are observed, the couple is increased, and the process continued. Let θ, φ be the angles subtended at the eye by the diameters in the plane of bending and perpendicular to it respectively. When the couple is increased, let these angles change to θ', φ' . Then Poisson's ratio is given by

$$\sigma = \frac{\frac{1}{\theta'} - \frac{1}{\theta}}{\frac{1}{\varphi'} - \frac{1}{\varphi}}.$$

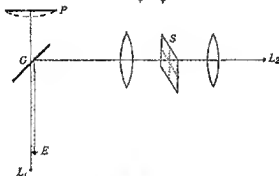


Fig. 24

The haloes are generally small and diffuse and do not improve when the plate is bent: great accuracy therefore cannot be attained.

24. Variation of Elasticity with Temperature.

For small ranges in the region of room temperature, there exists an approximately linear relation between elasticity and temperature. In general, as the temperature rises the elastic moduli fall, and for temperatures up to within 150° C. of the melting-point, Andrews† has found the general relation

$$q = q_1 e^{-bT},$$

where b takes some other value b_1 at an absolute temperature about half that of the melting-point. There is a general correlation

* Andrews, *Phil. Mag.* (2), Vol. 2, p. 345 (1925).

† Andrews, *Proc. Phys. Soc.*, Vol. 37, p. 3 (1925).

between degree of thermal expansion and change in the elastic modulus. Thus quartz, which has a negligible coefficient of expansion between 0° and 800° C., exhibits an almost constant value of q within this temperature range. Using a torsional oscillation method, Horton* has shown that the rigidity modulus, although showing approximately linear variation with temperature over small ranges, depends largely upon the previous treatment of the specimen. Irregular behaviour is also found at very low temperatures. The classical work of de Haas and Hadfield† has shown that the ductility of steel completely disappears at -252.8° C., whereas the mechanical properties of nickel, copper, and aluminium are much improved. In general, the effect is not permanent, the metal regaining its original elastic properties as the temperature returns to its original value.

25. Isothermal and Adiabatic Elasticities.

For small changes of temperature, the changes in the elastic properties of bodies are reversible; it is therefore possible to take e.g. a stretched wire through a Carnot cycle. Consider a wire of length l and cross-section A , subject to a strain e under a stress P and situated in a uniform temperature enclosure at a temperature T . Let the wire undergo an increase in strain δe ; the work done on the wire is $PAl\delta e$. Now let the wire be transferred to another uniform temperature enclosure at temperature $T + \delta T$, the elastic properties changing so that the stress becomes $P + \delta P$. Finally, let the wire contract until it regains its original strain e , after which it is brought back to the first temperature enclosure to complete the cycle. The work done by the wire at the higher temperature is

$$(P + \delta P)Al\delta e,$$

and hence the net work done by the wire is

$$\delta PAl\delta e.$$

If h represents the heat given out reversibly by the wire on being stretched at temperature T , by a well-known thermodynamical relation

$$\frac{\text{Net work done during cycle}}{\text{Heat given out at temperature } T} = \frac{\delta T}{T},$$

or

$$\frac{\delta PAl\delta e}{h} = \frac{\delta T}{T},$$

or

$$h = T \left(\frac{\delta P}{\delta T} \right)_{e, \text{ const}} Al\delta e.$$

* Phil. Trans., A, Vol. 204, p. I (1904)

† Phil. Trans., A, Vol. 232, p. 297 (1933)

If ρ is the density of the material of the wire, C its specific heat, and J the mechanical equivalent of heat, the change in temperature due to the elongation is then

$$\delta\theta = -\frac{T\left(\frac{\delta P}{\delta T}\right)_{\epsilon \text{ const.}}}{\rho C J} \delta\epsilon.$$

The change in strain $\delta\epsilon$ might have been produced by changing the temperature of the wire while maintaining the wire under constant stress. If α is the coefficient of linear expansion, the required temperature change is given by $\delta\epsilon = \alpha \delta T$. If we represent Young's modulus by q , the wire may be brought back to its original length by decreasing the stress by δP , where $\delta P = -q \delta\epsilon = -q \alpha \delta T$, or

$$\left(\frac{\delta P}{\delta T}\right)_{\epsilon \text{ const.}} = -q \alpha.$$

Hence $\delta\theta = -T q \alpha \delta\epsilon / (\rho C J)$. Now $q \delta\epsilon$ is the additional stress δP required to produce the change in strain $\delta\epsilon$. Hence the increase in temperature $\delta\theta$ produced by an increase in stress δP is given by

$$\delta\theta = -\frac{T \alpha \delta P}{\rho C J}. \quad \dots \dots \dots (46)$$

Equation (46) was first verified by Joule, using thermocouples inserted in loaded bars. A more recent application has been made by Bates and others to calibrate an apparatus used to measure changes of temperature in ferromagnetic rods undergoing short steps of magnetic hysteresis cycles.

In general, the increase in strain $\delta\epsilon$ due to the application of an increased strain δP is due partly to the increased stress and, if the heat does not escape, partly to the rise in temperature. The equation is

$$\delta\epsilon = \delta P / q + \alpha \delta\theta.$$

Now $\delta\theta$ is given by equation (46); hence

$$\delta\epsilon = \frac{\delta P}{q} - \frac{\alpha^2 T}{\rho C J} \delta P$$

or

$$\frac{\delta\epsilon}{\delta P} = \frac{1}{q} - \frac{\alpha^2 T}{\rho C J}.$$

If we denote the adiabatic value of Young's modulus by q' , we have

$$\frac{\delta \sigma}{\delta P} = \frac{1}{q'} = \frac{1}{q} - \frac{\alpha^2 T}{\rho C \beta}.$$

In agreement with theory, experiment shows that q' is always greater than q , but the numerical agreement is often far from satisfactory.

26 Rayleigh's Three Reciprocal Relations.

From consideration of the work done in elastic deformation under isothermal and adiabatic conditions, Rayleigh deduced three reciprocal relations;

(a) The displacement of a point B due to a force applied at A is equal to the displacement of a point A due to an equal force at B.

(b) If the point A be held fixed while B receives a displacement, the force required at A is equal to that required to hold B fixed when A receives an equal displacement.

(c) When a force is applied at A, and B is held fixed, the ratio which the reaction at B bears to the force at A is equal to the ratio which the displacement of A bears to the displacement of B, when a force acts at B while A is free from force.

To establish these (see Searle's *Experimental Elasticity*), the displacements x and y , in the direction of the forces X and Y , are given by $x = aX + cY$ and $y = cX + bY$, where a , b , and c are constants. Hence

(a) $y_{Y=0} = cX$ and $x_{X=0} = cY$, whence, if $X = Y$, $x_{X=0} = y_{Y=0}$.

(b) Solving for X and Y , and putting $x = y$, $X_{x=0} = Y_{y=0}$.

(c) Applying the conditions stated, $-Y_{y=0}/X_{x=0} = x_{x=0}/y_{y=0}$.

The validity of the relations can be tested by direct measurement of the quantities involved using a horizontal rod subjected to various loads and displacements.

27. Elastic Behaviour of Single Cubic Crystals.

The atomic theory of solids cannot yet claim the successes of the kinetic theory of gases described in Chapter IX, but systematic, if slow, advances are continually being made using an atomic interpretation; the study of the elastic behaviour of single crystals illustrates this. While it would be possible to measure the elastic constants of single crystals by static methods, it is more convenient and accurate to make use of dynamical relations established in Chapter VI. It is shown there that the velocity of propagation of waves through an elastic medium

obeying Hooke's law, is given by an expression of the form $v = (E/\rho)^{1/2}$, where ρ is the density of the medium and E is an elastic constant appropriate to the type and direction of the wave considered. Experimentally an ultrasonic pulse is generated by a quartz oscillator or *transducer*, and this pulse is transmitted through the crystal and reflected from the back face. The time which elapses between the original emission of the pulse and the arrival of the back-reflected wave is measured by standard electronic methods, and if the thickness of the crystal is known, the velocity of propagation follows directly. The frequency of the pulse is about 15 Mc./s. and the pulse duration is about 1 μ sec., the wavelength being about 3×10^{-4} cm. Specimens are about 1 cm. thick but the essential feature is the selection of specimens with accurately parallel faces and with faces orientated in a definite direction to the crystal axes.

Only cubic crystals will be considered here, but even with this restriction a variety of different bindings exists between the atoms composing the crystals, and these variations lead to corresponding variations in elastic behaviour. However, for all cubic crystals, a longitudinal wave will be propagated along a cube axis with a velocity given by $v_l = (g/\rho)^{1/2}$ where g is Young's modulus, while a shear wave will be propagated along the same axis with a velocity given by $v_s = (n/\rho)^{1/2}$ where n is the rigidity modulus. For directions of propagation other than along the cubic axes, the velocity of propagation of a shear wave is given by $v = (n/A\rho)^{1/2}$ where A is termed the *anisotropy factor*. For diamond with a shear wave along the 110 direction, A is 1.6 and the anisotropy arises from the fact that although the crystal is cubic, the forces between the carbon atoms are not independent of direction but are concentrated along four tetrahedral bond directions. In addition, for cubic crystals and central forces, an isotropic crystal should have $g/n = 3$, whereas for diamond the ratio is only about 2.1. Even for metals, a wide range of values of A exists, extending up to about 10, although tungsten is exceptional having A nearly unity. For the cubic alkali halides such as sodium chloride, where the forces between the atoms are ionic and therefore independent of direction (central), agreement is a little better with A about 0.7 although g/n is about 3.8.

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CHAPTER V

Compressibility of Solids and Liquids

1. Introduction. The Production of High Pressures.

The determination of the compressibility of liquids and solids presented for hundreds of years a problem of great experimental difficulty. In 1600, members of the Florentine Academy concluded that water was incompressible, since it was exuded through the pores of a hollow lead sphere when the latter was compressed in the jaws of a vice. Some years later Boyle demonstrated the compressibility of gases, communicating his results in a paper entitled "Touching the Spring of Air". Owing to the large magnitude of the effect in gases, work in this direction continued to progress satisfactorily.

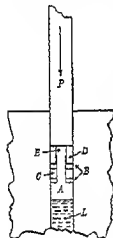


Fig. 1

(From Newman, *Recent Advances in Physics* (Churchill))

With liquids and solids, however, the effect is so small that it was not until 1762 that Canton first showed that water was definitely compressible. The experimental arrangement adopted was one which was used subsequently by the majority of experimenters until the recent work of Bridgman, when a new technique was devised. A large bulb fitted with a fine capillary is filled with the liquid, which is then subjected to pressure by a compression pump. The change in height of the liquid in the capillary indicates to a first approximation the change in the volume of the liquid. The method was developed by Regnault and is described in detail on p. 92.

The apparatus designed by Bridgman is shown in fig. 1. The liquid *L* is contained in a case of hardened steel, the pressure being applied by the advance of the steel piston *P*. The pressure is transmitted by the intermediary ring of steel *D* pressing on the soft rubber packing *C*, which is enclosed between the copper rings *B*, to the mushroom-shaped steel head *A* and thence to the liquid. The ingenuity of the apparatus lies in the fact that there can be no leak of liquid past the packing, since the pressure down the sides from above always becomes automatically greater than that up from the liquid. This action is achieved by

leaving a vacant space E behind the truncated stem of the head A ; the whole of the downward force must then be supplied by the pressure on the rubber rings C , and this pressure will be greater than that in the liquid in the ratio of the

which, by developing new ways of distributing stress and supporting critical parts, allow pressures up to 100,000 Kgm. per sq. cm. at temperatures of 2500° K. for hours of continuous operation.

2. Measurement of High Pressures.

(i) *Primary gauges.*

The other type of primary gauge is the free piston gauge which was introduced by Amagat. This consists of a piston which is accurately fitted to a cylinder so that the leak along the sides is unappreciable. The pressure is then measured directly from the load which must be applied to the top of the piston in order to maintain it in equilibrium. The joint between piston and cylinder may be luted with molasses, but this treatment is effective only up to a pressure of 3000 Kgm. per sq. cm. The piston is rotated just before a measurement is made, to eliminate the effect of friction.

(ii) *Secondary gauges.*

The simplest of these is the Bourdon spring gauge, which consists of a plane spiral of metal or glass tubing which is flattened at the closed end. When the pressure is transmitted down the tubing, the spiral tends to straighten out and a pointer may be made to register the pressure. The gauge is useful up to pressures of 4000–5000 Kgm. per sq. cm., its accuracy is limited by elastic hysteresis.

Bridgman has also used the variation of electrical resistance of a manganin coil with pressure as a secondary gauge. The method is particularly useful at high pressures.

3. Change in Volume of a Cylindrical Tube under Pressure.

As the change in volume of a cylindrical tube under pressure is involved in many determinations of the compressibility of solids and liquids, an expression for this quantity will now be obtained. Consider a cylindrical tube with flat ends, exposed to an external pressure p and an internal pressure P . Lamé has shown that the strains produced involve a radial displacement u given by

$$u = ar + \frac{b}{r} \quad (1)$$

at a point in the cylinder wall a distance r from the axis, α and β being constants. There is also a *longitudinal displacement* parallel to the axis of the cylinder.

If X , Y , Z are the normal stresses along the radius, tangential to it, and along the axis respectively, the corresponding strains being e_{xx} , e_{yy} , e_{zz} , reference to Chapter IV, section 6, p. 57, shows that

$$\left. \begin{aligned} X &= (K + 4n/3)e_{xx} + (K - 2n/3)(e_{yy} + e_{zz}) \\ Y &= (K + 4n/3)e_{yy} + (K - 2n/3)(e_{xx} + e_{zz}) \\ Z &= (K + 4n/3)e_{zz} + (K - 2n/3)(e_{xx} + e_{yy}) \end{aligned} \right\} \quad (2)$$

Now since $e_{xx} = d\sigma/dr$ and $e_{yy} = \sigma/r$, we have from (1)

$$e_{xx} = \alpha - \beta/r^2. \quad (3)$$

and

$$e_{yy} = \alpha + \beta/r^2. \quad (4)$$

Hence from (2), (3) and (4), at the limits r_1 and r_2 , where $X = -P$ and $X = -p$ respectively, we have

$$-P = 2K\alpha + 2n(\alpha - 3\beta/r_1^2)/3 + (K - 2n/3)e_{zz} \quad (5)$$

and

$$-p = 2K\alpha + 2n(\alpha - 3\beta/r_2^2)/3 + (K - 2n/3)e_{zz}. \quad (6)$$

Again, the force tending to stretch the cylinder parallel to its axis is $\pi(r_1^2 P - r_2^2 p)$, and the longitudinal stress is therefore

$$Z = \frac{(r_1^2 P - r_2^2 p)}{(r_2^2 - r_1^2)}. \quad (7)$$

From equations (2), (3) and (4), however,

$$Z = (K + 4n/3)e_{zz} + (K - 2n/3)2\alpha. \quad (8)$$

Hence, from (7) and (8),

$$\frac{r_1^2 P - r_2^2 p}{(r_2^2 - r_1^2)} = (K + 4n/3)e_{zz} + (K - 2n/3)2\alpha. \quad (9)$$

Finally, from equations (5), (6), and (9),

$$\alpha = e_{xx} = \frac{r_1^2 P - r_2^2 p}{(r_2^2 - r_1^2)} \frac{1}{3K} \quad (10)$$

and

$$\beta = \frac{r_1^2 r_2^2 (P - p)}{(r_2^2 - r_1^2)} \frac{1}{2n}. \quad (11)$$

The radial displacement σ is therefore given by

$$\sigma = \frac{r_1^2 P - r_2^2 p}{(r_2^2 - r_1^2)} \frac{r}{3K} + \frac{r_1^2 r_2^2 (P - p)}{(r_2^2 - r_1^2)} \frac{1}{2nr}. \quad (12)$$

If L is the length of the unstrained tube, its internal volume is originally $v_1 = \pi r_1^2 L$, and hence the approximate change in internal volume is

$$\delta v_1 = 2\pi r_1 \sigma L + \pi r_1^2 \epsilon_{xx} L, \quad \dots \quad (13)$$

since $\sigma = \delta r_1$ and $\epsilon_{xx} L = \delta L$.

From equations (10), (12) and (13) we have

$$\delta v_1 = \frac{\pi r_1^2 L}{(r_2^2 - r_1^2)} \left\{ \frac{r_1^2 P - r_2^2 p}{K} + \frac{r_2^2 (P - p)}{n} \right\}, \quad \dots \quad (14)$$

and the change in external volume δv_2 is similarly given by

$$\delta v_2 = \frac{\pi r_2^2 L}{(r_2^2 - r_1^2)} \left\{ \frac{r_1^2 P - r_2^2 p}{K} + \frac{r_1^2 (P - p)}{n} \right\}, \quad \dots \quad (15)$$

4. The Bulk Modulus of Solids.

The bulk modulus of solids may be determined as follows:

(i) Indirectly from the known relation (equation (5), Chapter IV, p. 59) between q , n and K , when q and n have been determined for the specimen. The disadvantage of the method is that the same specimen is rarely used for the determination of q and n and subsequently for the problem for which the value of K is required.

(ii) Many direct methods depend on the measurement of the strains of a thin hollow cylinder subject to given stresses. For example, Mallock has used an optical device to measure the longitudinal strain in a thin-walled tube under internal pressure. If the internal and external radii are r_1 and r_2 respectively, the pressure is P , and the longitudinal strain is l/L , from equation (10), putting $\epsilon_{xx} = l/L$ and p equal to zero, we have

$$K = \frac{Pr_1 L}{6l(r_2 - r_1)}, \quad \dots \quad (16)$$

since $(r_1 + r_2)$ is approximately equal to $2r_1$.

Alternatively, a load may be suspended from the end of the cylindrical tube arranged vertically and the change in internal volume registered by a liquid contained in the tube. The type of apparatus used by Amagat is shown in fig. 2; the change in volume is measured by means of the transparent graduated open capillary tube fixed to the top of the main tube. From equation (3), Chapter IV



Fig. 2

(p. 58), or the theory given in section 3 of this chapter (p. 89), the change in volume is given by

$$\frac{\delta v_1}{v_1} = \frac{P(1 - 2\sigma)}{q} = \frac{P}{3K} \quad \dots \quad (17)$$

where P is the applied stress, σ is Poisson's ratio, and $\delta v_1/v_1$ is the volume strain.



Fig. 3

(iii) Bridgman's methods are the most reliable; the general arrangement is shown in fig. 3.

A heavy steel cylinder PQ encloses the specimen AB , which is in the form of a rod. A uniform external pressure is then applied hydrostatically by immersing the cylinder in a high-pressure chamber (fig. 1), and the contraction l_2 of the rod relative to the cylinder is measured by the movement of a loose-fitting ring R_1 , which during the contraction moves to R_2 , in which position it remains after the pressure is removed. Owing to the extension in length l_2 of the cylinder, the true contraction of the rod is given by $l = l_1 - l_2$. The change in length of the cylinder, which is only a few per cent of the change in the rod, is determined by comparator measurements. The volume strain is then given by $3l$, since the method actually measures the longitudinal strain. In place of the ring recorder R_1, R_2 , a sliding contact may be used, the change in length being determined in terms of a change in electrical resistance.

The absolute compressibility of one metal, for example iron, having been determined, relative and hence absolute compressibilities of other materials may be rapidly obtained.

In fig. 4, the specimen in the form of a long rod S is kept pressed against the bottom of the holder of iron by the spring At . Attached to the upper end of the rod is a high-resistance wire sliding over a contact D , attached to the holder but insulated from it. The spring N keeps the wire pressed against its contact.

The relative position of holder and wire is determined by a potentiometer measurement of the difference of potential between the sliding contact D and a terminal E fixed to the wire. One current terminal is at F and the other is earthed to the apparatus. The whole arrangement is placed in a high-pressure chamber and exposed to hydrostatic pressure; the relative linear compressibility is directly determined from the change in resistance.



Fig. 4

(From Bridgman, *The Physics of High Pressure* (Bell).)

5 Compressibility of Liquids.

(i) *Older Experiments.*—The early experiments are of historical interest only, owing to the uncertainty in the correction for the change of volume of the containing vessel. The instruments as a whole are termed *piezometers*. If δv_1 is the apparent change in volume of the liquid contained in a piezometer under a pressure P applied simultaneously internally and externally, the true contraction will be

$$\delta v = \delta v_1 + \delta v_2, \quad \dots \quad (18)$$

where δv_2 is the decrease in the internal volume of the container. For a cylinder of isotropic material, with flat ends, we obtain from equation (14), putting $p = P$,

$$\frac{\delta v_2}{v_1} = \frac{P}{k}, \quad \dots \quad (19)$$

and hence if k has been determined for the material by an independent experiment, δv_2 may be calculated. Finally, if K is the bulk modulus of the liquid, its value will be given by

$$\frac{\delta v_1}{v_1} = P \left(\frac{1}{K} - \frac{1}{k} \right). \quad (20)$$

The method has been used by Regnault and others

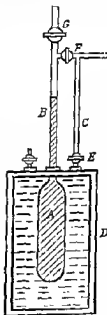


FIG. 5

compression pump and manometer. The pressure is transmitted to the outside of A by liquid contained in the outer vessel D , which can be placed in communication with the compressor by the side-tube C and the tap F . This tap, together with the remaining taps F and G , allows the pressure to be communicated (1) to the outside only, (2) to the inside only, or (3) to the outside and inside simultaneously. While the last arrangement is all that is required to obtain K from equation (20), if δv_0 and δv_1 represent the apparent contractions in volume under conditions (1) and (2), it may easily be shown, by applying equations (14) and (20), that

$$\delta v_0 + \delta v_1 = \delta v_2, \quad (21)$$

if the container is truly isotropic; a useful check on the applicability of equation (20) is therefore provided. In Regnault's experiments the container was actually a cylinder with rounded ends, and the corrections to be applied to equation (20) are of doubtful validity.

(ii) *Bridgman's Experiments.*—The classical experiments on the

compressibility of liquids and the standard pressure-volume isothermals are due to Bridgman.

The liquid is contained in a steel cylinder similar to that shown in fig. 1, but fitted with an accurately-fitting steel piston carrying a contraction-measuring ring *B*, exactly like that shown in fig. 3 for the experiments on solids. The arrangement is then immersed in a high-pressure chamber of the type described on p. 87 the pressure being registered by means of a manganin resistance. The whole apparatus is placed in a thermostat; for water, isothermals up to 80° C. were obtained. To correct for the expansion of the containing vessel, the liquid is partially replaced by steel and the combined compressibility of the two is obtained.

6. Behaviour of Solids and Liquids at High Pressures.

The properties of matter at very high pressures are of fundamental importance, since atomic changes may be expected when forces of the order of the interatomic forces are applied. Pressures of 10^5 Kgm. per sq. cm. would be required to produce large effects: up to the present the maximum pressure attained is about 20,000 Kgm. per sq. cm., but even before this value is reached many interesting phenomena have been observed. A few of the more important observations of Bridgman will now be tabulated.

(1) Change in volume is entirely reversible with pressure; up to 25,000 Kgm. per sq. cm. no permanent change is produced.

(2) With liquids the volume change becomes relatively smaller; the compressibility at 12,000 Kgm. per sq. cm. is only about 1/20 of its value at moderate pressures.

(3) The coefficient of thermal expansion decreases, but to a lesser extent than the compressibility, and at very high pressures the same value is approached by all liquids.

(4) While a large part of the compressibility of liquids (and gases) is due to a decrease in the space between the atoms, with solids almost all the change of volume is produced by actual shrinkage of the atoms. The compressibility of solids is irregular, some decreasing and others increasing with increasing pressure.

(5) Anisotropic solids exhibit a great difference in the compressibilities along the different crystal axes. Tellurium actually expands along the trigonal axis when a uniform hydrostatic pressure is applied.

(6) There is no critical point between liquid and solid, and no maximum melting-point temperature above which only the liquid phase can exist, no matter how high the pressure.

(7) The coefficient of viscosity increases, and at enormously different rates for different substances. The approximate relation is $\eta = n \log p$, where n is a constant depending on the nature of the substance.

(8) The elastic moduli of some solids increase, while those of others decrease.

(9) The effect on thermal conductivity is irregular. Out of 48 metals, 39 show a decrease in electrical resistance; thermoelectric properties vary in both directions, while the Wiedemann-Franz ratio between thermal and electrical conductivities* increases in 9 examples out of 11. This behaviour indicates that the connexion between thermal and electrical conductivities cannot be completely explained on the existing electronic theory of metals and that there must be a considerable difference in the electron mechanisms giving rise to electrical resistance and thermoelectric effects.

(10) Caesium is the most compressible solid, the volume reducing to about $\frac{2}{3}$ at 100,000 Kgm. per sq. cm.

(11) Most sudden changes in compressibility are due to a change in the crystal lattice but examples are known where a reduction in the size of the electron orbits can be produced by external pressure.

(12) The transition graphite to diamond is irreversible if the material is cooled to room temperature before the pressure is reduced.

7. Fixed Points and the Construction of a Pressure Scale.

The measurement of absolute pressure beyond about 13,000 Kgm. per sq. cm. is very difficult. Mercury manometers are obviously impractical, and the limit of the ordinary free-piston gauge has been reached. However, by making use of certain constant physical properties, a pressure scale is being constructed with the aid of fixed points, the number of which is continually increasing. Typical among these are the freezing pressures of mercury, 7640 and 13,700 Kgm. per sq. cm. at 0° and 36° C. respectively. Another point is the transition of bismuth I to bismuth II at 25,000 Kgm. per sq. cm. This point is marked by a discontinuity in the bismuth compressibility curve; it is not critical with respect to temperature. The manganin resistance gauge is then calibrated against the two mercury points and the bismuth point, and the change of resistance is expressed as a quadratic function of the pressure, the relation being almost linear over the initial portion of the range. In some experiments with sodium chloride Bridgman estimated the pressure at 200,000 atmospheres; such estimates involve wide extrapolations of the pressure curve and are liable to errors exceeding 20 per cent. For certain crystalline substances, the fundamental theory of which is fairly well developed, assistance is provided from a theoretical estimate based on calculations of ionic and interatomic forces.

In the manufacture of diamonds, pressures in the highest regions were calibrated by making use of four of the electrical resistance transitions up to 80,000 Kgm. per sq. cm. established by Bridgman for Bi, Ti, Cs, and Ba at 25,400, 45,000, 55,000 and 80,000 respectively. For pressures above 80,000 Kgm. per sq. cm. the melting-point of Ge

* See Roberts, *Heat and Thermodynamics* (Blackie), fourth edition, p. 289

CHAPTER VI

Seismic Waves

1. Introduction.

Seismology deals with the problem of ascertaining the structure of the earth by means of the various waves which are produced by earthquakes. The source of these waves is the *focus* of the earthquake, that is, the place where the earth actually undergoes fracture. This region is some distance below the surface of the earth. The nearest point of the earth's surface to the focus is called the *epicentre*. By means of instruments called *seismographs*, records of the vibrations propagated from the focus to various points on the earth's surface are made. Great progress has been made in detecting and analysing these records and in assigning causes to the various types of vibrations.

2. Velocity of Longitudinal Waves.

After an earthquake has occurred, the first signal recorded by seismographs at distant stations is that due to the so-called *primary* or *P* wave (fig. 1). In this type of wave the vibrations are longitudinal,

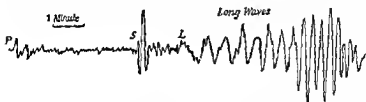


Fig 1

that is, the particles of matter of which the earth is composed vibrate along the line of propagation of the energy. If the earth were a homogeneous sphere, these vibrations would travel along rectilinear paths, starting at the focus of the earthquake. The path between focus and recording station would be a chord of a great circle of the earth. In " " book, this elementary view of the situation is adopted, and the velocity of the *P* waves through a homogeneous earth is calculated.

Consider the body undergoing strain, mentioned on p. 56. As in Chapter IV, p. 58, the three equations (1) hold, namely,

$$\begin{aligned}P_1 &= \lambda\delta + 2n'e_{xx}, \\P_2 &= \lambda\delta + 2n'e_{yy}, \\P_3 &= \lambda\delta + 2n'e_{zz},\end{aligned}$$

where

$$\lambda = \frac{\sigma q}{(1+\sigma)(1-2\sigma)} \quad \text{and} \quad 2n' = \frac{q}{(1+\sigma)}. \quad (1)$$

Here q is Young's modulus of elasticity, σ is Poisson's ratio, and n' is n , the modulus of rigidity; e_{xx} , e_{yy} , e_{zz} are the strains and P_1 , P_2 , P_3 the stresses along the three axes respectively; and $\delta = e_{xx} + e_{yy} + e_{zz}$.

Consider the special case in which the only strain is $e_{xx} = \delta$ along the x -axis, e_{yy} and e_{zz} being each equal to zero. In this case P_1 , the stress along the x -axis, is equal to $\lambda e_{xx} + 2n'e_{xx}$.

That is,

$$\begin{aligned}P_1 &= e_{xx}(\lambda + 2n) \\&= e_{xx} \left\{ \frac{\sigma q}{(1+\sigma)(1-2\sigma)} + \frac{q}{(1+\sigma)} \right\}, \quad (2)\end{aligned}$$

$$= \frac{e_{xx} q (1-\sigma)}{(1+\sigma)(1-2\sigma)}, \quad (3)$$

$$= j e_{xx}, \text{ say,}$$

$$\text{where} \quad j = \frac{q(1-\sigma)}{(1+\sigma)(1-2\sigma)}. \quad (4)$$

The coefficient j is called the *elongational elasticity*. As equation (3) shows, it is the modulus or factor connecting P_1 and e_{xx} when e_{yy} and e_{zz} are each equal to zero. In other words, equation (4) represents the relation between the stress and the strain in any direction, when lateral strains perpendicular to the first are prohibited. Now these are precisely the circumstances which arise when a longitudinal wave-train passes through a homogeneous medium which is practically unlimited in lateral directions. They are in sharp contrast with the circumstances attending the passage of longitudinal waves along a rod or wire.

Let a train of longitudinal waves of the above type traverse a homogeneous medium (fig. 2). Consider the forces on an element of matter AB , of uniform density ρ and unit cross-section, displaced longitudinally along the axis Ox to CD . Let the medium be unlimited laterally.

Let the displacement AC be L . Then BD is the same function of

$x + dx$ as l is of x . By Taylor's theorem, $f(x + dx) = f(x) + f'(x)dx$, if we neglect small terms. Here $BD = f(x + dx) = l + \frac{\partial l}{\partial x} dx$. Hence CD , which is equal to $BD - BC$, is equal to

$$l + \frac{\partial l}{\partial x} dx - l + dx = dx \left(\frac{\partial l}{\partial x} + 1 \right).$$

Hence $CD - AB$, which is the extension of the element AB due to its displacement, is equal to $(\partial l / \partial x) dx$. The fractional extension is $\partial l / \partial x$. By equation (3) the average tensile force on the element CD is $j(\partial l / \partial x)$. If, however, equal tensions acted on the element at C and D , no longitudinal waves would be propagated. One tension must exceed the other. Only a small error of the second order is made by assuming $j(\partial l / \partial x)$ to be the tension at one end of the element CD ,

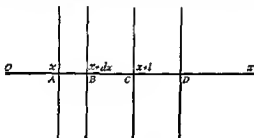


Fig. 1

say at C . The value of the tension at D is the same function of $x + dx$ as $j(\partial l / \partial x)$ is of x . Hence, by Taylor's theorem, it is

$$j \frac{\partial l}{\partial x} + j dx \frac{\partial^2 l}{\partial x^2},$$

approximately. At C the force on the element CD is $j(\partial l / \partial x)$, towards the origin O . At D the force is

$$j \frac{\partial l}{\partial x} + j dx \frac{\partial^2 l}{\partial x^2},$$

away from the origin. Now the mass of the element is ρdx . Applying Newton's second law of motion to the element, we have

$$j dx \frac{\partial^2 l}{\partial x^2} = \rho dx \frac{\partial^2 l}{\partial t^2}$$

or

$$\frac{\partial^2 l}{\partial t^2} = \frac{j}{\rho} \frac{\partial^2 l}{\partial x^2} \quad \dots \dots \dots (5)$$

This type of differential equation is well known under the title of the "wave equation". A general solution of it is $l = \text{any function of } (x - v_1 t) = f(x - v_1 t)$, say, where

$$v_1^2 = j/\rho. \quad \dots \dots \dots (6)$$

This means that longitudinal waves travel along the x -axis with velocity

$$v_1 = \left(\frac{j}{\rho}\right)^{\frac{1}{2}} = \left\{\frac{g(1-\sigma)}{\rho(1+\sigma)(1-2\sigma)}\right\}^{\frac{1}{2}}. \quad \dots \dots (7)$$

In a homogeneous earth, P waves would have this velocity. The adjectives *primary*, *irrotational*, *condensational*, and *push*, as well as *longitudinal*, are applied to these waves. In practice three distinct sets of P waves, arising in different ways, are often observed in the seismographic record of a single earthquake.

3. Velocity of Transverse Waves.

The second section of the vibrations recorded by distant seismographs after an earthquake is due to the so-called *secondary* or S waves (fig. 1). These vibrations have no component in the direction of propagation: they are transverse vibrations. In a homogeneous earth they too would pursue rectilinear paths starting at the focus of the earthquake, that is, chords of great circles. It will now be shown that the velocity of such transverse waves in homogeneous matter of density ρ is $v_2 = \left(\frac{n}{\rho}\right)^{\frac{1}{2}}$, where n is the modulus of rigidity.

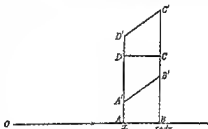


Fig. 3

Assume that the particles of matter vibrate in planes perpendicular to the direction of propagation, in rectilinear paths. Even if a transverse vibration is elliptical or circular, it can be resolved into two perpendicular rectilinear vibrations. Let Ox be the direction of propagation of a transverse plane wave (fig. 3). Consider a slice of matter $ABCD$ of thickness dx , normal to Ox . When a plane wave passes along, let every particle in the plane AD undergo the same lateral displacement in the plane of the figure, so that A goes to A' and D to D' . Let $AA' = DD' = y$. Similarly, let every particle in the plane BC undergo a lateral displacement $y + dy$. In this case $BB' = CC' = y + dy$. In such circumstances the slice undergoes shearing in the

y -direction. The angle of shear is $\theta = \frac{\partial y}{\partial x}$
by the thickness
p. 55, the average
is $n \frac{\partial y}{\partial x}$. I

AD and BC , a static shear would ensue, but no propagation of waves. Waves are propagated when there is a greater tangential force on one face, say on $B'C'$, than on $A'D'$. Assume, as a close approximation to the truth, that the tangential force per unit area acting on $A'D'$ is $n \frac{\partial y}{\partial x}$, which is a function of x . This acts in the direction DA' . The force per unit area acting on $B'C'$ is the same function of $x + dx$ as $n \frac{\partial y}{\partial x}$ is of x . Hence it is given by $f(x + dx) = f(x) + f'(x)dx$, approximately, where $f(x) = n \frac{\partial y}{\partial x}$; that is, $f(x + dx) = n \frac{\partial y}{\partial x} + n dx \frac{\partial^2 y}{\partial x^2}$, approximately. This force acts in the direction $B'O'$. The net force per unit area tending to displace the slice in the y -direction is the difference $n dx \frac{\partial^2 y}{\partial x^2}$. Let the length AD be 1 cm. and let the thickness of the slice perpendicular to the plane of the figure also be 1 cm. Then the mass of the element $ABCD$ is ρdx . Its equation of motion in the y -direction, derived from Newton's second law, is

$$\rho dx \frac{\partial^2 y}{\partial t^2} = n dx \frac{\partial^2 y}{\partial x^2},$$

which reduces to

$$\frac{\partial^2 y}{\partial t^2} = \frac{n}{\rho} \frac{\partial^2 y}{\partial x^2}, \quad \dots \dots (8)$$

where t represents time.

This is a partial differential equation of the second order, of the same form as equation (5). A general solution of it is

$$y = f \left\{ x - \left(\frac{n}{\rho} \right)^{\frac{1}{2}} t \right\},$$

where f means any function. This can be written in the form

$$y = f(x - v_s t), \quad \text{where } v_s = \left(\frac{n}{\rho} \right)^{\frac{1}{2}}. \quad \dots (9)$$

This equation represents a disturbance travelling in the positive direction of x with velocity $v_s = \left(\frac{n}{\rho} \right)^{\frac{1}{2}}$. The adjectives *secondary*, *equi-voluminal*, *distortional* and *shake* are also applied to these waves as well as the adjective *transverse*. In practice the S waves arrived at the observing station in a direction inclined at some angle to the horizontal

It is customary to consider the component vibrations in (a) the horizontal direction (the *SH* waves) and (b) the vertical plane containing the direction of propagation (the *SV* waves). Three different types of *S* waves, arising in different ways, are usually recorded in the seismogram of a single earthquake.

It may be noted that $v_s = \left(\frac{\pi}{\rho}\right)^{\frac{1}{2}}$ is the expression for the velocity of transverse waves in any homogeneous elastic solid, and thus represents the velocity of light through the ether of space according to Fresnel's elastic solid theory. In that case π and ρ are the modulus of rigidity and the density of the ether respectively.

4. Rayleigh Waves.

There is a third type of wave, discovered by Lord Rayleigh, in which the vibrations are confined to a relatively thin layer close to the surface of the earth. In this case the waves do not arrive at the observing station along a chord starting from the focus of the earthquake, but along a great circle starting from the epicentre. Further, the displacement of particles of matter at any point on the earth's surface is in the vertical plane containing the direction of propagation, and can be resolved into (a) a vertical component, (b) a horizontal component in the direction of propagation. There is no horizontal component normal to the direction of propagation. No other kind of wave transmitted along the earth's surface would persist over long distances. The calculation of the velocity of Rayleigh waves is too long to reproduce here,* but it may be stated that the velocity would be constant if the earth were homogeneous. In the real earth, composed as it is of heterogeneous layers, a disturbance starting out as a single pulse becomes dispersed, that is, broken up into a set of waves with various periods and wave-lengths, all travelling with different velocities. At distant observing stations a series of oscillations is recorded, instead of a single throw such as would be observed if the earth were homogeneous.

5. Love Waves.

In the real heterogeneous earth a fourth type of surface waves, the Love waves, exists, in which the displacements of the particles of matter are horizontal and transverse to the direction of propagation. At any point on the earth's surface after an earthquake, a series of oscillations corresponding to Love waves of various velocities is produced. It can be deduced, from the fact that these waves actually exist, that their velocity is less in the surface layer of the earth's crust than in the subjacent matter. In actual seismograms recorded at distant stations the arrival of the *P* and *S* waves is well marked, but

* See Jeffreys, *The Earth* (Cambridge University Press).

the *S* wave is followed by a long series of oscillations, as in fig. 1. These are due to the Rayleigh and Love waves intermingled, and their complete interpretation is not yet settled. These complicated vibrations are referred to as the *long* or *L* waves, or as the *main shock*.

6. Seismographs.

The purpose of a seismograph is to register movements of the ground at the place where the instrument is situated. Any vibration of the ground may be resolved into three components, (a) vertical, (b) horizontal (say east and west), (c) horizontal (say north and south). Components (b) and (c) are of the same type, so that the problem is to record vertical and horizontal vibrations.

We first consider horizontal vibrations. To record these, one general method is to use some kind of pendulum, formed by a body suspended from a stand resting on the ground. It is instructive to consider the theory of the vibrations of a rigid "vertical" pendulum, when the ground and therefore the stand and the point of support are displaced horizontally.

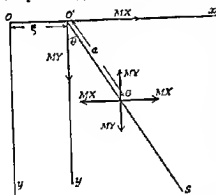


Fig. 4

Case 1.—Friction neglected

Let *O'GS* (fig. 4) represent a rigid pendulum vibrating about a horizontal axis through *O'*, perpendicular to the plane of the figure. By the horizontal displacement of the ground, *O'* itself has undergone a horizontal displacement ξ to the right, from a fixed point *O*. Let (*x*, *y*) be the co-ordinates of the centre of gravity *G*, referred to fixed axes *Ox*, *Oy*. Then $x = \xi + a \sin \theta$, $y = a \cos \theta$, where a is the length of the pendulum. The forces acting on the pendulum are (a) the weight *Mg*, acting

of eq

to the

MX

body

ward

equations of motion of the pendulum are

neglect friction, are

$$M\ddot{x} = MX \text{ and } M\ddot{y} = Mg + MY.$$

Hence

$$\ddot{x} = X \text{ and } \ddot{y} = g + Y. \quad (10)$$

Taking moments about G , we obtain the equation of rotatory motion, namely,

$$MK^2\ddot{\theta} = MY(x - \xi) - MXy.$$

Hence

$$\begin{aligned} K^2\ddot{\theta} &= Yx \sin\theta - Xx \cos\theta \\ &= (\bar{y} - y)x \sin\theta - \bar{x}x \cos\theta, \quad \dots \dots (11) \end{aligned}$$

from (10), where K is the radius of gyration of the pendulum about an axis through its centre of gravity G . Now since

$$\begin{aligned} x &= \xi + a \sin\theta, \\ \bar{x} &= \xi + a(\cos\theta \cdot \bar{\theta} - \sin\theta \cdot \dot{\theta}). \end{aligned}$$

Assume that θ is small and that $\dot{\theta}$ is negligibly small. Then

$$\bar{x} = \xi + a \cos\theta \cdot \bar{\theta}. \quad \dots \dots (12)$$

Further, y is approximately constant and $\bar{y} = 0$. Equation (11) becomes

$$K^2\ddot{\theta} = -g\bar{\theta} - a\xi'' - a^2\ddot{\theta}. \quad \dots \dots (13)$$

Hence

$$(K^2 + a^2)\ddot{\theta} + g\bar{\theta} + a\xi'' = 0. \quad \dots \dots (14)$$

Let $(K^2 + a^2)/a = l$; l is the distance between O' and a certain point O , called the *centre of oscillation*. Then

$$l\ddot{\theta} + g\bar{\theta} + \xi = 0. \quad \dots \dots (15)$$

Put $g/l = n^2$. Then

$$\ddot{\theta} + n^2\bar{\theta} + \frac{\xi}{l} = 0. \quad \dots \dots (16)$$

The actual displacement ξ due to a distant earthquake is usually a complicated function of the time, but by Fourier's theorem it may be supposed to be resolved into a series of cosine terms, each of the form $\xi = \xi_0 \cos \omega t$. Taking one of these terms, we insert $\xi = \xi_0 \cos \omega t$ in equation (16). It becomes

$$\ddot{\theta} + n^2\bar{\theta} - \frac{\omega^2 \xi_0 \cos \omega t}{l} = 0.$$

Hence

$$\ddot{\theta} + n^2\bar{\theta} = \frac{\omega^2 \xi_0 \cos \omega t}{l}. \quad \dots \dots (17)$$

The complete solution of this involves the complementary function and the particular integral. The complementary function is the solution of

$$\ddot{\theta} + n^2\bar{\theta} = 0,$$

which is

$$\bar{\theta} = A \cos(nt + \varphi).$$

The particular integral is found by writing

$$(D^2 + n^2)\bar{\theta} = \frac{\omega^2 \xi_0 \cos \omega t}{l},$$

whence

$$\bar{\theta} = \frac{\omega^2 \xi_0 \cos \omega t}{l(n^2 - \omega^2)}. \quad \dots \dots (18)$$

The complete solution is

$$\bar{\theta} = A \cos(nt + \varphi) + \frac{\omega^2 \xi_0 \cos \omega t}{l(n^2 - \omega^2)}. \quad \dots \dots (19)$$

As the second term is the one produced by the earthquake, it is more interesting to us than the first. Write

$$\theta_1 = \frac{\omega^2 \xi_0 \cos \omega t}{l(n^2 - \omega^2)},$$

since $\xi = \xi_0 \cos \omega t$, we have

$$\xi = \frac{\theta_1 l(n^2 - \omega^2)}{\omega^2} \quad \dots \dots \dots (20)$$

This represents one of the Fourier terms into which the actual displacement has been resolved. If a style or pen is mounted at the end *S* of the pendulum, such that *OS* = *L* cm., the apparent linear displacement of the style is *Lθ*, approximately, of which *Lθ*₁ is due to the earthquake.

$$\begin{aligned} L\theta_1 &= \frac{L\omega^2 \xi_0 \cos \omega t}{l(n^2 - \omega^2)} \\ &= \frac{L\omega^2 \xi}{l(n^2 - \omega^2)} \quad \dots \dots \dots (21) \end{aligned}$$

where $\xi = \xi_0 \cos \omega t$. The total displacement of the style is *Lθ* + ξ .

Case 2.—Friction taken into account

Assume that a frictional force is present, which is proportional to the angular velocity of the pendulum. Insert a term of the form *aθ̇* to represent this retarding force, in equation (14). On reducing to the form of equation (16), and writing the frictional term as 2*λθ̇*, we obtain the equation

$$\ddot{\theta} + 2\lambda\dot{\theta} + n^2\theta + \frac{k}{l} = 0. \quad \dots \dots \dots (22)$$

Again assume that the actual seismic displacement ξ of the support can be expanded by Fourier's theorem in a series of cosine terms of the form $\xi = \xi_0 \cos \omega t$. Substitute $\xi = \xi_0 \cos \omega t$ in equation (22). It becomes

$$\ddot{\theta} + 2\lambda\dot{\theta} + n^2\theta = \frac{\omega^2 \xi_0 \cos \omega t}{l}. \quad \dots \dots \dots (23)$$

As before, the complementary function represents that part of θ which is not produced by seismic displacements. To find the particular integral, assume a solution of the form $\theta = \theta_0 \cos(\omega t - \varphi)$. On substituting in equation (23) we have

$$-\omega^2 \theta_0 \cos(\omega t - \varphi) - 2\lambda \omega \theta_0 \sin(\omega t - \varphi) + n^2 \theta_0 \cos(\omega t - \varphi) = \frac{\omega^2 \xi_0 \cos \omega t}{l},$$

which is true for all values of *t*. Substitute $\omega t = \frac{\pi}{2}$; then

$$(-\omega^2 + n^2) \sin \varphi = 2\lambda \omega \cos \varphi$$

and

$$\tan \varphi = \frac{2\lambda \omega}{n^2 - \omega^2} \quad \dots \dots \dots (24)$$

Now put $\omega t = \varphi$. Then

$$(-\omega^2 + n^2)\theta_0 = \frac{\omega^2 \xi_0 \cos \varphi}{l} \quad \text{and} \quad \theta_0 = \frac{\omega^2 \xi_0 \cos \varphi}{l(n^2 - \omega^2)}.$$

From equation (24),

$$\cos \varphi = \frac{(n^2 - \omega^2)}{\{ (n^2 - \omega^2)^2 + 4k^2 \omega^2 \}^{\frac{1}{2}}}$$

and

$$\theta_0 = \frac{\omega^2 \xi_0}{L \{ (n^2 - \omega^2)^2 + 4k^2 \omega^2 \}^{\frac{1}{2}}} \quad \dots \quad (25)$$

The case when $k=n$ is of practical importance; for example, Galitzin's seismographs utilize this critical value of the damping. Then equation (25) becomes

$$\theta_0 = \frac{\omega^2 \xi_0}{L(n^2 + \omega^2)} \quad \dots \quad (26)$$

The quantity θ_0 , which is the apparent maximum displacement of the centre of oscillation due to one Fourier term of the seismic displacement, is equal to

$$\frac{\omega^2 \xi_0}{n^2 + \omega^2} \quad \dots \quad (27)$$

that is, equal to ξ_0 multiplied by a constant factor. A pen at a distance L from the point of support or knife-edge has the apparent maximum displacement $L\theta_0$, which is also proportional to ξ_0 . The pen faithfully reproduces the movements of the support with the same frequency, but on a different scale, provided the support moves with a definite frequency and amplitude for a sufficient number of oscillations. The magnification is the ratio of the pen's displacement to that of the support or ground. For a displacement $\xi = \xi_0 \cos \omega t$, the magnification is $L\theta_0/\xi_0$ (comparing maximum displacements). This is equal to $L\omega^2/(n^2 + \omega^2)$ in the important case of critical damping.

7. Horizontal Pendulum Seismograph (Galitzin).

Seismographs belonging to the class of vertical pendulums just discussed are actually used to measure horizontal displacements, velocities, and accelerations of the earth's crust. They have, however, the disadvantage of being very heavy. Pendulums with masses up to 20 tons are required in order to reduce the friction involved in the registration of vibrations, when great magnification is needed. Another disadvantage is that the period of oscillation is small. To avoid these defects, seismographs belonging to the class of horizontal pendulum described in Chapter II, p. 35, are frequently used to measure horizontal movements.* The student should therefore refer to pp. 35-37 before proceeding further. Only slight additions are required to convert a horizontal pendulum into a very sensitive seismograph. When the earth moves horizontally, the supports of the pendulum do likewise and the "boom" of the latter is set in motion.

Various types of recording device are in use. In Galitzin's method, the boom of the horizontal pendulum extends beyond the bob. At a point on it beyond the bob a flat coil of copper wire is mounted, so that when the boom moves the coil moves in a strong magnetic field produced by a pair of horseshoe magnets. An induced current proportional to the angular velocity of the boom is produced in the coil, which is connected to a very sensitive galvanometer. The movements of the suspended part of the galvanometer are recorded by means of the usual

* For details of seismographs for measuring vertical displacements, see e.g. *Handbuch der Experimentalphysik*, Vol. XXV, Part II (1931).

time of the explosion is noted. Seismographs situated at other points *A, B, C* and *D*, all in one plane, record the times of arrival of the first *P* waves. T_1, T_2, T_3, T_4 are measured. Should one mean veloc



FIG 6

velocity along the other paths. Similar measurements in a direction perpendicular to the first, using waves from a fresh source, confirm the first results. A more detailed survey then enables the position of the top and flanks of the dome to be accurately ascertained.

11. The Reflection Method of Seismic Prospecting.

At the boundary between two kinds of rocks, an incident wave

bed is properly located by him when he knows (a) the length of the perpendicular SN drawn from S to the plane, (b) the angle of dip ϕ of the plane, i.e. the angle which a straight line of deepest descent XNY, in the plane and passing through N, makes with its own projection X'SA in a horizontal plane, (c) the direction of that horizontal projection N'S; to the section ting or

Correlation Shooting

This form of reflection method is used when the beds of rock to be located have extensive plane upper faces and low dip. The apparatus used includes a number of receivers arranged at regular intervals along a straight line on one side of a point called the "shot point", at which an explosion is arranged to take place. Fig. 7 represents such a system. S is the shot point and $R_1, R_2, \dots R_6$ are six receivers with equal spacing

α . When the shot is fired at S , longitudinal seismic waves pass downwards and are reflected by the upper plane XY of the bed to be located, whose nature differs from that of the rock above it. Consider the simple case when the normal SN and all the ray paths $ST_1, T_1R_1, ST_2, T_2R_2, \&c.$, are coplanar straight lines. The time taken by the various reflected waves to reach $R_1, R_2, \&c.$, can be calculated as follows. Let S' be the image of the shot point in the plane XY , regarding XY as a plane mirror. SNS' is normal to the plane. Let $SN = NS' = p$

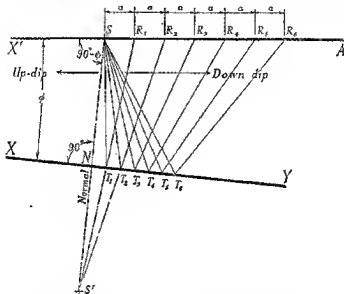


Fig. 7

and let $SR_1 = R_1R_2, \&c., = \alpha$. (α is of the order 20-100 ft.) Let $\phi =$ angle of dip of the plane XY . From the geometry of the figure it is seen that $NSR = 90 + \phi$. Also $ST_1 + T_1R_1 = S'R_1$, and $ST_2 + T_2R_2 = S'R_2, \&c.$ Let v be the velocity of the waves, and let $2p = P$. Then the distance traversed by the waves from the shot point to the first receiver is $ST_1 + T_1R_1 = S'R_1$. From the trigonometry of the triangle $SS'R_1$,

$$\begin{aligned} S'R_1 &= \{S'S^2 + SR_1^2 - 2SS' \cdot SR_1 \cdot \cos(90 + \phi)\}^{\frac{1}{2}} \\ &= \{P^2 + \alpha^2 + 2Pa \sin \phi\}^{\frac{1}{2}}, \end{aligned}$$

and the travel time t_1 taken by the waves to go from S to R_1 via T_1 , is

$$t_1 = S'R_1/v = \{P^2 + \alpha^2 + 2Pa \sin \phi\}^{\frac{1}{2}}/v$$

$$\text{or} \quad v^2 t_1^2 = P^2 + a^2 + 2Pa \sin \phi, \text{ where } P = 2p. \quad (30)$$

Quite generally, if there are n receivers, then

$$v^2 t_n^2 = P^2 + (na)^2 + 2P \cdot na \cdot \sin \phi. \quad (31)$$

The times are measured by six receivers, the interval $t_n - t_1$ sometimes being as large as 0.04 sec. Keeping in mind the object of the measurements which is to find $p = P/2$ and ϕ or $\sin \phi$, a general method would be to write $P^2 = X$ and $P \sin \phi = Y$. The six equations would take the form

$$X + 2naY + n^2a^2 - v^2 t_n^2 = 0 \text{ after rearranging.}$$

To find the most probable values of X and Y in these circumstances, one of the methods of § 6, Chapter XII, would be needed. It is simpler and sufficiently accurate to adopt alternative methods.

First Method.

The method of least squares and the like are sometimes too laborious for the practical geophysicist. He may prefer a less accurate and shorter method. In one of these let the distance SR from shot point to a receiver be x . Suppose the receiver to be on the "down-dip" side of S. If the travel time of the reflected waves from shot point to receiver is t_1 , then, as in equation (30),

$$v^2 t_1^2 = 4p^2 + x^2 + 4px \sin \phi. \quad (32)$$

Next, if a receiver is placed at the same distance x from the shot point, but on the "up-dip" side of S, the travel time t_2 is given by

$$v^2 t_2^2 = 4p^2 + x^2 - 4px \sin \phi. \quad (33)$$

On adding (32) and (33), we get after rearranging

$$4p^2 = v^2(t_1^2 + t_2^2)/2 - x^2, \quad (34)$$

so that p can be calculated from measured values of v , t_1 , t_2 , and x . Thus

$$p = \{v^2(t_1^2 + t_2^2)/8 - x^2/4\}^{1/2}. \quad (35)$$

On subtracting (32) from (33), we get after rearranging

$$8px \sin \phi = v^2(t_1^2 - t_2^2)$$

$$\text{and} \quad \sin \phi = v^2(t_1^2 - t_2^2)/8px. \quad (36)$$

Writing $t_1 + t_2 = 2t$ and $t_1 - t_2 = \Delta t$, we get

$$\sin \phi = v^2 \cdot t \cdot \Delta t / 4px. \quad (37)$$

Here $t = (t_1 + t_2)/2$ is the average time and $\Delta t = t_1 - t_2$ is the difference of the times. Equations (35) and (37) give p and ϕ in terms of measurable quantities.

Second Method.

The following method is sometimes used to combine the measurements of times made by a pair of down-dip receivers at distances x_1 and x_2 from the shot point. In this case two equations of the same kind as (32) hold, giving

$$v^2 t_1^2 = 4p^2 + x_1^2 + 4px_1 \sin \phi, \quad . \quad . \quad . \quad (38)$$

$$v^2 t_2^2 = 4p^2 + x_2^2 + 4px_2 \sin \phi. \quad . \quad . \quad . \quad (39)$$

It is left to the student to prove that

$$p^2 = \{v^2(t_1^2 x_1 - t_2^2 x_2) + x_1^2 x_2 - x_2^2 x_1\} / 4(x_1 - x_2) \quad . \quad (40)$$

$$\text{and} \quad \sin \phi = \{v^2(t_1^2 - t_2^2) / (x_1 - x_2) - (x_1 + x_2)\} / 4p. \quad . \quad . \quad (41)$$

Therefore to get $\sin \phi$ we must use in equation (41) the value of p derived from equation (40).

These exact expressions for p^2 and $\sin \phi$ are frequently replaced by approximate formulæ when ϕ is small.

Continuous Profiling.

The second reflection method, called "continuous profiling", is applied when the dip is small and the reflecting beds are not so well defined over large areas. In this case, the shot point S and receivers R_1 to R_6 are first arranged as for correlation shooting and the shot is fired. Times are measured. The shot point is then moved to R_6 , the position of the sixth receiver, which is moved back to S . Thus, when a shot is fired, reception is carried out in the reverse direction (see fig. 8). In this way almost twice as many reflections as before are obtained from a given portion $T_1 T_{11}$ of the upper face of the bed. $T_1 T_{11}$ is, so to speak, examined more closely than before.

The double process is next applied to the portions of the reflecting plane adjacent to $T_1 T_{11}$ either on the down-dip or up-dip side. By proper arrangement of the receivers, "holes", i.e. unexamined portions of the plane left under the shot points, may be eliminated or made small. The spacing a is generally from 100 to 150 feet.

Dip Shooting.

A third reflection method, called "dip shooting", is used when the angle of dip is large and when the reflecting beds are not so well

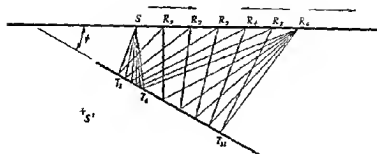

 $+R'_4$

FIG 8

defined over large areas. It has several forms. One is the same as the continuous profiling method. Another form involves shooting once in each hole with half the receivers on one side and half on the other side. A series of shots is taken with the shot points and receivers distributed along a closed loop enclosing a considerable area of the district. In this way the underground structures can be mapped systematically.

A typical example of the disposition of such beds is shown in the graph in fig. 9 which expresses the results of a survey made by the Bohlen gravimeter (p. 26). A layer of the heavy mineral pyrrhotite, 7-8 metres thick, was known to be below the surface of the ground

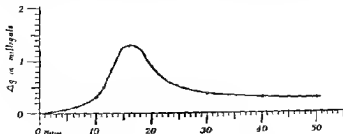


FIG 9

at Kärrobo, Sweden. Values of Δg were measured along a straight line on the earth's surface, crossing over the so-called "ore body", and using the first point as a standard position. Ordinates are values of Δg in milligals; abscissæ are distances measured from the first point.

12. Constitution of the Earth.

Studies of the behaviour of seismic waves, together with advances in geomagnetism, geology and geochemistry, have recently led to a marked increase in our knowledge of the structure of the earth itself. There is some probability that the earth consists of four layers, termed the *crust*, the *mantle*, the *core*, and the *central body*. The radius of a true sphere equal in volume to the earth is 6371 km., and the mean density is 5.517 gm./c.c. The crust of the real earth is the outermost layer and it is composed of two comparatively thin sub-layers. According to Jeffreys, the surface layer is composed of solid rocks of a granitic nature, of mean thickness about 11 km. and mean density 2.65 gm./c.c. The lower sub-layer, sometimes termed the intermediate solid layer, is of mean thickness 24 km., and mean density 2.87 gm./c.c. and probably partly consists of basaltic rocks. These two layers together compose the crust, and the fact that both P and S type seismic waves are reflected at the base of the intermediate layer is evidence for a discontinuity at the base of the crust. Below the crust, and composed of rocks akin to olivine, is the thick solid mantle, whose internal radius is about 3500 km., that is, its inner boundary is about 2900 km. below the earth's surface. When seismic P and S waves, coming from the focus of an earthquake, strike this boundary, both sets undergo reflection, but while the P waves are also transmitted, the S waves are not. Thus no S wave has been found to pass forward into the core. There is therefore a sharp discontinuity at a depth of about 2900 km. which is regarded as due to a change from solid to liquid in a downward direction, since liquids cannot transmit S waves. Supporting evidence for this is afforded by a study of the lunar bodily tide within the earth, as it is only possible to account for the amplitude of this tide by assuming the core to be liquid. There is strong evidence that the magnetic field observed at the surface of the earth is generated in the core, which is rotating more slowly than the mantle.

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CHAPTER VII

Capillarity

I. Elementary Principles.

It is assumed here that the student already has some elementary knowledge of capillary phenomena. The customary view is adopted, namely, that in every surface film separating a liquid and a gas, two liquids, or a solid and a liquid, a surface tension exists. This is defined as the force per centimetre exerted in the tangent plane to the surface, in a direction normal to an element of a line drawn in that surface through any point. This quantity is assumed to have the same value at every point in a given film, whatever the shape of the film may be. From a second point of view the surface tension is also the "free" or "available" energy, in the thermodynamic sense, of one square centimetre of film surface. This definition is equivalent to the first since, if a portion of film, one centimetre wide, is extended so as to increase the area by one square centimetre, employing a force equal to the surface tension defined in the first manner, acting through one linear centimetre, the work done is equal to that surface tension. By reversing the process and letting the film contract, an amount of energy, equal to the work done previously, is now released by the film, and hence the second definition follows. According to the problem under discussion, use is made, sometimes of one, sometimes of the other, definition.

When a liquid and a solid meet along some line, a certain angle is included inside the liquid between a tangent plane to the surface of the liquid and a tangent plane to the surface of the solid at any point on the curve of contact. It is known as the *angle of contact* of that particular liquid and solid. The measured value of an angle of contact, and indeed of surface tension, depends on various conditions:

(a) Whether the liquid is advancing, receding, or at rest on the solid. (This has been called a hysteresis effect.)

(b) Whether the solid is covered by a complete layer of matter foreign to itself, i.e. by a contamination film.

(c) Whether the liquid is contaminated in any other way. (The surface of the liquid should be swept clean before measurements are made.)

(d) On the interval of time (the time of immersion) in which the liquid and solid have been in contact.

(e) On the amount of friction between solid and liquid.

Measurements of angles of contact have meaning only if a quantitative account of these conditions of observation is given.

Theorem.—The excess of pressure on one side of a film of constant surface tension over that on the other side is equal to $T(1/R_1 \pm 1/R_2)$, where T is the surface tension, and R_1, R_2 are the principal radii of curvature of the film at the point in question.

Proof.—Consider a surface film separating two regions containing fluids (fig. 1). In general it will be curved. Let a small curvilinear

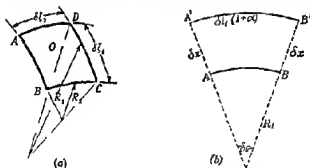


FIG. 1

rectangle be drawn, enclosing any point O in the film, such that the sides are in "principal sections" of the film passing through A, B, C and D , the film being regarded as a geometrical surface.* Let the sides

* The two principal sections at a point are such that the curves of section have maximum and minimum radii of curvature

one side of the film over that on the other side. Let the film, pushed forward by the excess pressure p , undergo a small displacement δx cm. along the outward normal through O . As a result of this displacement, let the sides of the rectangle be increased from δl_1 to $\delta l_1(1 + \alpha)$ and from δl_2 to $\delta l_2(1 + \beta)$ respectively, where α and β are small compared with unity. Thus the area of the rectangle is increased, and as this involves stretching of the film, work is done against the surface tension. Since the system was initially in equilibrium, it can be assumed that the work done by the excess pressure in pushing back the film is equal to the work done in stretching it. After the stretching, the new area of the element of film is

$$\delta l_1(1 + \alpha) \delta l_2(1 + \beta) = \delta l_1 \delta l_2(1 + \alpha + \beta + \alpha\beta).$$

If we neglect the small term $\alpha\beta$, we have $\delta l_1 \delta l_2(1 + \alpha + \beta)$. The initial area was $\delta l_1 \delta l_2$, so that the increase in area is $\delta l_1 \delta l_2(\alpha + \beta)$ sq. cm. Referring to fig. 1, we see that $\delta l_1(1 + \alpha) = (R_1 + \delta x) \delta \theta$ and also $\delta l_1 = R_1 \delta \theta$, so that $\alpha = \delta x/R_1$. Similarly, $\beta = \delta x/R_2$. Hence the increase in area is

$$\delta x \delta l_1 \delta l_2 \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \text{sq. cm.}$$

If we assume, as in elementary work, that the surface tension R may also be defined as the work required to stretch a surface film by one square centimetre under isothermal conditions,* and if we further assume that the stretching in the present case is isothermal, the work required to stretch the patch of film by the above amount is

$$T \delta x \delta l_1 \delta l_2 \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \text{ergs.}$$

Now consider the work done by the excess pressure p in pushing forward the elementary area of film through δx cm. The initial thrust on the patch of film is the excess pressure multiplied by the area, i.e. $p \delta l_1 \delta l_2$ sq. cm. The final thrust is $p \delta l_1 \delta l_2(1 + \alpha + \beta)$. As α and β are small compared with unity, we may assume the thrust to be constant and equal to $p \delta l_1 \delta l_2$. When a force of this magnitude advances its point of application through δx cm., the work done is $p \delta x \delta l_1 \delta l_2$ ergs. Equating the two quantities of work and cancelling factors, we have

$$p = T \left(\frac{1}{R_1} + \frac{1}{R_2} \right). \quad \dots \dots \dots (1)$$

* Strictly speaking, this definition requires correction by the theory of § 34, p. 172.

If the centres of curvature of the sides AB and BC are on opposite sides of the film and if $R_1 < R_2$, the equation has the form

$$p = T \left(\frac{1}{R_1} - \frac{1}{R_2} \right). \quad \dots \quad (2)$$

2. Shape of an Interfacial Boundary.

Consider a system of two incompressible liquids in contact and in equilibrium, the lighter one resting on the heavier. Fig. 2 represents a principal section of such a system; the curve AB is a section of the surface of contact. It is required to find an equation for the curve AB .

Take a point O far below the interface as origin of co-ordinates, and axes Ox , Oy . Let the interface undergo an elementary virtual displacement in which each element of surface moves from its initial position

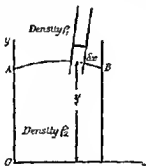


FIG. 2

to its final position along a normal to itself, the displacement at a point P being δn cm. Let the element of surface have sides of length δl_1 and δl_2 cm., and let $\delta l_1 + \delta l_2 = \delta S$. Let the excess pressure on the concave side be p dynes per sq. cm. Then, as in the last theorem, this pressure gives rise to a force $p\delta S$ dynes, which does work on the element of interface amounting to $p\delta S\delta n = p\delta V$ ergs, where $\delta V = \delta S\delta n$ is an element of volume.

By the last theorem this work is equal to $T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta V$ ergs, where R_1 and R_2 are the principal radii of curvature at P . The sum of all such quantities taken over the whole of the interface is

$$\iiint T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) dV \text{ ergs.}$$

As a result of the displacement, the system gains or loses potential energy. The gain of energy may be calculated as follows. Let the initial vertical co-ordinate of the typical element of surface just considered be y . Since the liquids are incompressible, the liquid removed from any one region is replaced by an equal volume from another. The displacement of the surface, δn , has the following effective result so far as gravitational potential energy is concerned. An element of volume δV of mass $\rho_1 \delta V$, with vertical co-ordinate y , is removed from its initial position and replaced by an element of volume δV of mass $\rho_2 \delta V$ with the same co-ordinate y . This particular element of volume gains potential energy $(\rho_2 - \rho_1)gy\delta V$ ergs, and the total gain of energy is

$$\iiint (\rho_2 - \rho_1)gy dV \text{ ergs,}$$

the integration being taken over the whole of the interface. Since the system is initially in equilibrium, the work done by the hydrostatic pressure is equal to the gain in potential energy. Hence

$$\iiint T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) dV = \iiint (\rho_2 - \rho_1)gy dV;$$

that is,

$$\iiint \left\{ T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) - (\rho_2 - \rho_1)gy \right\} dV = 0.$$

Now $\iiint dV$, which represents the total volume change of the system, is zero, since the liquids are incompressible; hence

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) - (\rho_2 - \rho_1)gy = \text{a constant,} \quad . \quad . \quad (3)$$

an equation which may be regarded as the differential equation of the surface whose section is AB .

The above reasoning holds in the case when one of the media is an incompressible liquid and the other a gas, for $\iiint dV$ will still be zero.

If we put $\rho_2 - \rho_1 = \rho$, we obtain equation (3) in a convenient form,

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) - g\rho y = \text{constant.} \quad . \quad . \quad (4)$$

Equation (4) is of great importance and forms the basis of many of the particular problems elucidated in the following sections.

3. Rise of a Liquid along the Side of an Inclined Plane Plate.

Let AB represent a transverse section of one face of a plane plate dipping into a liquid (fig. 3). The plate may be supposed to be of

infinite length in the direction perpendicular to the plane of the figure. *BEC* represents a principal section of the free surface of the liquid. Assume that it is horizontal at a great distance from the plate. Let the angle of contact of the liquid with the plate be ψ , that is, let *DB*, the tangent to the curve *BEC* at the point of contact *B*, make an angle ψ with the plate. If we take an origin *O* below the surface, as in the last section, the equation of the curve *BEC* is

$$T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) - g\rho y = \text{constant}, \quad \dots (5)$$

where $\rho = \rho_2 - \rho_1$ and the other symbols have their previous meanings. In the present problem all sections of the surface parallel to the plane

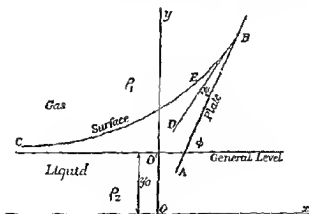


Fig. 3

of the figure are similar in shape, that is, the surface is cylindrical and one radius of curvature is infinite. Equation (5) therefore becomes

$$\frac{T}{R} = g\rho y + \text{constant}. \quad \dots (6)$$

If we take *O*, in the "general level" of the free surface at a great distance from the plate, as origin, the constant becomes zero, for when $y = 0$ the free surface is plane and *R* is infinite.

Consider the tangents *PL*, *QM* and normals *PS*, *QS* drawn at *P* and *Q*, two points on the curve, an elementary distance δs apart (fig. 4). Let the ordinate of *P* be *y*. Let the tangents make angles θ and $\theta + \delta\theta$ with the axis *Ox*. The normals meet at *S*, the centre of

curvature. The angle $PSQ = \delta\theta$, $PS = QS = R$, and $PQ = \delta s$. From the figure $R\delta\theta = \delta s$; hence $1/R = \delta\theta/\delta s$ and

$$\frac{T}{R} = T \frac{\delta\theta}{\delta s} = g\rho y.$$

Now

$$\frac{\delta y}{\delta s} = \sin \theta, \quad \text{and} \quad \frac{1}{\delta s} = \frac{\sin \theta}{\delta y};$$

hence

$$T \frac{\delta\theta}{\delta s} \delta y = T \sin \theta \delta\theta = g\rho y \delta y.$$

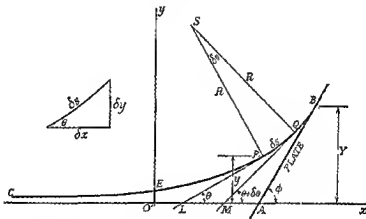


Fig. 4

On integration we have

$$-T \cos \theta = \frac{1}{2} g\rho y^2 + \text{constant},$$

that is,

$$g\rho y^2 + 2T \cos \theta = \text{constant}.$$

When $y = 0$, $\theta = 0$, $\cos \theta = 1$, hence the constant is $2T$. That is,

$$g\rho y^2 = 2T(1 - \cos \theta). \quad \dots \dots (7)$$

This is the equation of the curve BEC.

Comments.

(1) If the plate makes an angle ϕ with the horizontal, a tangent to the curve at B, where the liquid meets the plate, makes an angle $(\phi - \psi)$ with the horizontal (ψ is the angle of contact), and the vertical co-ordinate Y of B is given by

$$g\rho Y^2 = 2T\{1 - \cos(\phi - \psi)\}. \quad \dots \dots (8)$$

(2) (a) If the plate is vertical, $\phi = 90^\circ$, and

$$gpY^2 = 2T(1 - \sin \phi). \quad (9)$$

(b) If $\phi = 0$ in addition,

$$gpY^2 = 2T. \quad (10)$$

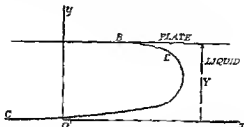


FIG. 5

(3) The general reasoning still holds if the plate is horizontal and the liquid is attached to the lower face; in fig. 5, for example, at a point of contact B we have $\phi = 180^\circ$. Hence

$$gpY^2 = 2T(1 + \cos \phi).$$

When

$$\phi = 0, gpY^2 = 4T.$$

(4) The expression T/gp is often called Laplace's constant* and is expressed by a^2

(5) When a "sessile" drop or bubble, resting on or pendent from a horizontal plate, is large (fig. 6), a central portion of its surface, $HXYZ$, does not depart appreciably from the cylindrical shape, and the equation to a profile curve for a central section such as MN is given approximately by equation (8) with $\phi = 180^\circ$.

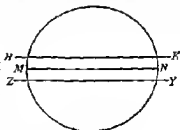


FIG. 6—Plan of large sessile drop or bubble

4. Rise of a Liquid between Parallel Vertical Plates.

Let fig. 7 represent a vertical section of a system in which a liquid rises between two vertical parallel plates. The angle of contact is not assumed to be zero. The profile curve $ACPB$ is the same in all parallel sections perpendicular to the plates, and the surface of the liquid is cylindrical, i.e. one radius of curvature is infinite. Take an origin O in the general level of the external liquid, midway between the plates, and take horizontal and vertical axes Ox, Oy . The theory of § 3, p. 119, applies here; if y is the vertical co-ordinate of any point P on the profile curve, equation (5) holds, giving

$$T(1/R_1 + 1/R_2) - gpy = \text{constant, where } \rho = \rho_2 - \rho_1.$$

* Among the authors who use $T/gp = a^2$ are Ferguson, Rayleigh, and Dorsey. Among those who prefer $2T/gp = a^2$ are Sisson, Adams, and Lenard.

As in § 3, one radius is infinite and the origin lies in the general level, so that the equation becomes $T/R = g\rho y$.

From fig. 4, p. 121, we have $R\delta\theta = \delta s$. Further, $\delta y = \delta s \sin \theta$, hence $T \delta y/R = T \sin \theta \delta\theta = g\rho y \delta y$.

Integrating, we have $-T \cos \theta = \frac{1}{2}g\rho y^2 + \text{constant}$.

At C let $y = y_0$ and $\theta = 0$; then $-T = \frac{1}{2}g\rho y_0^2 + \text{constant}$.

By subtraction $2T(1 - \cos \theta) = g\rho(y^2 - y_0^2)$, . . . (11)

which can be written $y^2 = \frac{2T}{g\rho}(B - \cos \theta)$, . . . (12)

where $B = 1 + g\rho y_0^2/(2T)$.

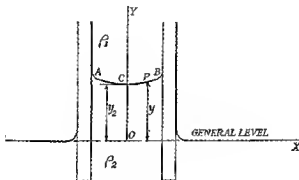


Fig. 7.

The profile curve $ACPB$ may either be concave or convex upwards or it may have a point of inflection, according as the liquid makes an acute angle of contact with both plates, with neither, or with one plate only. Thus when the constant B of equation (12) exceeds $+1$, y^2 is positive, and y may be either positive or negative, but not zero. The equation then gives the profile curve when the liquid makes an acute angle of contact with both or neither of the plates.

Equation (12) is the differential equation of the profile curve. A rigorous integration is difficult, but the co-ordinates of various points can be obtained by a method of successive approximation, of which a sketch is now given.

At C (fig. 8), the radius of curvature is given by equation (6), that is, $T/R_0 = g\rho y_0$ or $R_0 = T/g\rho y_0$.

Near C , it may be assumed that an elementary portion CD of the profile curve is circular and of radius R_0 . Let K be the centre of this circle; then $KC = KD$. Let CKD be a small angle 2ϕ .

In fig. 8,

$$CE = FD = CD \cos \phi = 2R_0 \phi \cos \phi,$$

$$DE = CD \sin \phi = 2R_0 \phi \sin \phi.$$

The ordinate of D is $y_0 + DE$

$$= y_0 + 2R_0 \phi \sin \phi.$$

If $y = y_0 + 2R_0 \phi \sin \phi$ is now substituted in the equation $T/R = g\rho y$, a value of $R = R_1$, say, is obtained, which may be taken as the radius of curvature of the next element DH of the profile curve. Thus

$$R_1 = \frac{T}{g\rho(y_0 + 2R_0 \phi \sin \phi)}$$

By an argument similar to the one used in obtaining DE and CE , the increments DG and GH may now be found:

$$DG = 2R_1 \phi \cos 2\phi \text{ and } GH = 2R_1 \phi \sin 2\phi.$$

To obtain the relation between the ordinates of the points of contact, we proceed as follows. Let the liquid make angles of contact Q_1, Q_2 with the plates on the left and right respectively, and let the ordinates of the points of contact be Y_1 and Y_2 respectively.

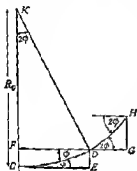


FIG. 8

By equation (11),

$$g\rho(Y_1^2 - y_0^2) = 2T(1 - \cos \theta_1) = 2T(1 - \sin Q_1),$$

$$g\rho(Y_2^2 - y_0^2) = 2T(1 - \cos \theta_2) = 2T(1 - \sin Q_2).$$

By subtraction we obtain

$$g\rho(Y_1^2 - Y_2^2) = 2T(\sin Q_2 - \sin Q_1), \quad (13)$$

which is the required relation.

5. Rise of a Liquid between Two Parallel Vertical Plates close together.

In determining the height of the lowest point of the surface, let us assume the plates (fig. 9) to be of the same material, the angle of contact to be zero, and the distance between the plates to be X cm., where X is very much less than a , that is, than $\sqrt{T/g\rho}$. As the plates are close together and the length of the profile curve is small, it may be assumed to be semicircular. The elevated portion of the liquid is in equilibrium. Consider a column of it, 1 cm. thick, measured at right angles to the plane of fig. 9. The downward force on it, i.e. its weight, is equal to the sum of the two upward forces due to surface

tension. The area between the sections of the meniscus and the tangent plane at its lowest point is equal to the area of a rectangle minus the area of a semicircle, that is, its area is $X^2/2 - \pi X^2/8$.

Hence the volume of the slice of unit thickness is

$$Xy_0 + \frac{X^2}{2} - \frac{\pi X^2}{8}.$$

The equation of equilibrium is

$$\text{Weight of slice of unit thickness} = 2T,$$

or

$$Xy_0 g \rho + g \rho X^2 \left(\frac{1}{2} - \frac{\pi}{8} \right) = 2T;$$

hence

$$y_0 = \frac{2T}{X \rho g} - 0.107 X, \quad \dots \dots (14)$$

which is the required height. It is left to the student to calculate y_0 when the angle of contact is not zero.

6. Horizontal Force on One Side of a Vertical Plane Plate Dipping in a Liquid.

Take an origin O in the general level (fig. 10). Let the liquid under consideration extend indefinitely to the left of the figure. Take any point K on the left-hand face of the plate; let OK be y . Consider the horizontal force on an elementary area of the plate, whose section is $KQ = \delta y$, and whose length, measured at right angles to the plane of the paper, is 1 cm. Since K is y cm. above O , the pressure there is the atmospheric pressure P minus the quantity gpy ; accordingly, the force on KQ towards the right is $(P - gpy)\delta y$ dynes. On the whole surface up to A , where $OA = Y$, the whole force acting horizontally to the right is

$$\int_0^Y (P - gpy) dy = PY - \frac{1}{2} g \rho Y^2 \text{ dynes.}$$

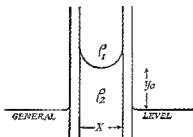


Fig. 9

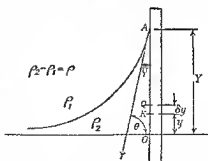


Fig. 10

Further, at the top there is a force $T \sin \phi$ acting horizontally to the left, where ϕ is the angle of contact. The resultant force to the left is $T \sin \phi - PY + \frac{1}{2} g \rho Y^2$ dynes.

Now by equation (9), p. 122,

$$g \rho Y^2 = 2T(1 - \sin \phi).$$

Hence the net force to the left is $T - PY$, provided we neglect any forces acting on the plate above A .

7. Horizontal Force on One of Two Parallel Vertical Plates Dipping in a Liquid.

In fig. 11 let the point K be y cm. above the general level. If the atmospheric pressure is P , the pressure at K is $P - gpy$. Consider

the forces on a strip of plate of height δy between two horizontal planes LQ and MK , per centimetre length measured at right angles to the plane of the figure. On LM there is a force $P \delta y$ dynes to the right. On QK there is a force $(P - gpy) \delta y$ dynes to the left. The net force is therefore $gpy \delta y$ dynes to the right. The total

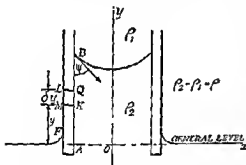


Fig. 11

force of this kind acting on the plate to the right up to the level of B is $\int_0^Y gpy dy$ dynes, where $Y \approx AB$, that is, $\frac{1}{2} g \rho Y^2$ dynes. If the angle of contact at B is ϕ , there is another force $T \sin \phi$ acting to the right, making $\frac{1}{2} g \rho Y^2 + T \sin \phi$ altogether. Outside the plate and acting to the left, there is a force which by the theory of the previous section is $T - PZ$, where Z is the height of the point F . If, as usually happens, Z is negligible compared with Y , this force reduces to T . Hence, if we take into consideration forces both inside and outside, the resultant force acting to the right is

$$\frac{1}{2} g \rho Y^2 + T \sin \phi - T \text{ dynes.} \quad \dots \dots (15)$$

8. Rise of a Liquid in a Vertical Circularly Cylindrical Tube. (Narrow Tube: Angle of Contact not Zero.)

Fig. 12 represents a central vertical section of a circularly cylindrical tube dipping into a liquid. The profile or meridional curve is represented by LMN . Let the angle of contact be ψ . In the present case of a narrow tube the profile curve is short in length and may be assumed to be nearly circular, that is, the surface may be assumed to be nearly spherical.*

Let $\rho = \rho_2 - \rho_1$. Let r and R be the radii of the tube and of the meniscus respectively, and let H be the height of M , the lowest point of the meniscus, above the general level. It is assumed that the same atmospheric pressure P exists above the liquid inside and outside the tube. Since the elevated portion of the liquid is in equilibrium, its weight is equal to the upward force due to surface tension, acting around the circle whose section is LN . Hence

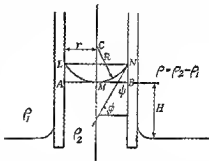


Fig. 12

$$2\pi r T \cos \psi = \pi r^2 H \rho g + \text{weight of liquid lens between } LMN \text{ and } AMB. \quad (16)$$

If the weight of the liquid lens is neglected, equation (16) reduces to

$$2\pi r T \cos \psi = \pi r^2 H \rho g,$$

whence

$$T = \frac{r H \rho g}{2 \cos \psi}.$$

When the volume of the liquid lens $LMNBA$ is not negligible, it is calculated by elementary mensuration and is found to be

$$V = \pi r^3 \left\{ \sec \psi + \frac{2}{3} \tan^3 \psi - \frac{2}{3} \sec^3 \psi \right\},$$

expressed in terms of the angle of contact and the radius of the tube. In this case the equation of equilibrium is

$$2\pi r T \cos \psi = \pi r^2 H \rho g + \pi r^3 \rho g \left\{ \sec \psi + \frac{2}{3} \tan^3 \psi - \frac{2}{3} \sec^3 \psi \right\},$$

which gives

$$T = \frac{rH\rho g}{2 \cos \psi} + \frac{r^2 \rho g}{2} \left\{ \sec^2 \psi + \frac{2}{3} \sec \psi \tan^3 \psi - \frac{2}{3} \sec^4 \psi \right\}.$$

When

$$\psi = 0, \quad T = \frac{rH\rho g}{2} + \frac{r^2 \rho g}{6}.$$

If we put $T/\rho g = a^2$, we may write this equation in the form

$$H = \frac{2a^2}{r} - \frac{r}{3}. \quad \dots \dots \dots (17)$$

9. Rise of a Liquid in any Vertical Circularly Cylindrical Tube Dipping into an Open Vessel of Liquid (Angle of Contact not Zero).

Fig. 13 represents a central vertical section. The surface of the liquid is not assumed spheroidal, nor is the profile curve assumed circular. By symmetry, however, the surface must be a surface of revolution.

Equation of the Meridional Profile Curve.—Take an origin O at the point where the axis of the tube meets the general level. The vertical co-ordinate y of any point P is given by equation (4) of § 2, namely,

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) - g\rho y = \text{constant}, \quad \dots \dots (18)$$

where in this case neither R_1 nor R_2 is infinite. One of these principal radii is the radius of curvature of the meridional profile curve. Let it be R_1 .

The other principal radius R_2 is equal to PC , where PC is the normal at P , because of the symmetry about the axis OO . Thus $R_2 = PC = x/\sin \phi$, where $MCP = \phi$.

Further, if we note that at M , which is one of those points which in solid geometry are known as umbilics, the radii of curvature are equal, they may each be denoted by b , say, and if we put $OM = Y$, equation (18) becomes

$$\frac{2T}{b} - g\rho Y = \text{constant} \quad \dots \dots \dots (19)$$

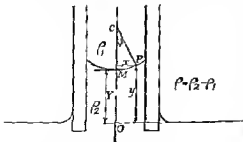


Fig. 13

Hence at any point P , by equations (18) and (19), we have

$$T \left(\frac{1}{R_1} + \frac{\sin \phi}{x} \right) - g\rho y = \frac{2T}{b} - g\rho Y. \quad (20)$$

Divide throughout by T/b and put $y - Y = z$, then

$$\frac{1}{R_1/b} + \frac{\sin \phi}{x/b} = 2 + \frac{z\rho g}{T/b}. \quad (21)$$

Write $T/g\rho = a^2$ and

$$\frac{b^2}{a^2} = \frac{b^2 g\rho}{T} = \beta. \quad (22)$$

Then

$$\frac{1}{R_1/b} + \frac{\sin \phi}{x/b} = 2 + \frac{\beta z}{b}. \quad (23)$$

If R_1 and $\sin \phi$ are expressed in terms of x and z , this equation takes the form of a differential equation of the second order, which has not yet been integrated by rigorous methods. However, Bashforth and Adams* devised a special method of obtaining numerical values of x/b and z/b corresponding to various values of ϕ from 0° to 180° and of β from $+0.1$ to $+100$. To use the important tables published by them, values of β and ϕ are chosen and then the tables give the corresponding values of x/b and z/b . The value of x/b fixes that of β , and vice versa.

10. Application to the Measurement of Surface Tension.

Sugden† has described what some authorities regard as the best form of the capillary rise method of obtaining surface tensions of liquids in the presence of their own vapours. He makes the substitution $2T/g\rho = a_1^2$. The theoretical part of the determination involves three cases, (1) $r/a_1 < 0.25$, (2) $0.25 < r/a_1 < 2.24$, (3) $r/a_1 > 4.24$. There is a hiatus between (2) and (3), referred to again on p. 131.

We begin by considering the second case.

Case (2), $0.25 < r/a_1 < 2.24$. The liquid is placed in a vertical U-tube (fig. 14) with one narrow limb and one wide limb, the radii being r_1 and r_2 respectively. Further, $0.25 < r/a_1 < 2.24$ for the

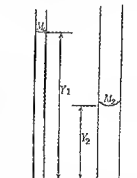


Fig. 14

* *An Attempt to Test the Theory of Capillary Action* (Cambridge University Press, 1883).

† Sugden, *Journ. Chem. Soc.*, Vol. 119, p. 1483 (1921).

narrow limb. The limbs are regarded as two separate tubes standing in an open vessel. We see that equation (5) or (19) holds for each umbilic, that is,

$$\frac{2T}{b_1} - g\rho Y_1 = \text{constant},$$

$$\frac{2T}{b_2} - g\rho Y_2 = \text{the same constant},$$

where b_1, b_2 are the radii of curvature at the points M_1, M_2 and Y_1, Y_2 are the heights.

On subtraction,

$$2T\left(\frac{1}{b_1} - \frac{1}{b_2}\right) = g\rho(Y_1 - Y_2) = g\rho H, \text{ say.} \quad (24)$$

Tube (1) is narrow and tube (2) is wide. As a first approximation, put $b_1 = r_1$ and $b_2 = \infty$; then, if we use the measured value of H , which is easy to obtain, an approximate value of $2T/g\rho = a_1^2$ is calculated.

From the measured values of r_1 and r_2 , r_1/a_1 and r_2/a_1 are calculated.

Assume that the angle of contact, ψ , of the liquid has been measured; ψ is 90° minus the ϕ of Bashforth and Adams, when the point P is on the line of contact of liquid and tubes, and their tables give the corresponding β .

Now, by the definition of a_1 , equation (22) becomes

$$\frac{2b^2}{a_1^2} = \beta; \quad (25)$$

hence

$$\frac{1}{a_1} \sqrt{\frac{2}{\beta}} = \frac{1}{b},$$

and

$$\frac{r}{a_1} \sqrt{\frac{2}{\beta}} = \frac{r}{b} \quad (26)$$

Sugden has constructed a table of corresponding values of β , r/b , and r/a_1 obtained from equation (26), for values of r/a_1 between 0.25 and 2.24.

Using the approximate values of r_1/a_1 and r_2/a_1 obtained above, Sugden's table gives values of r_1/b_1 and r_2/b_2 , and hence $1/b_1$ and $1/b_2$ are calculated. Substitute these new values of $1/b_1$ and $1/b_2$ in equation (24) and calculate a more accurate value of $2T/g\rho = a_2^2$ and hence of r_1/a_2 and r_2/a_2 values of r_1/b_1 and r_2/b_2 value of a_2^2 and a_2 . After of a_1

obtained becomes practically constant and an accurate value of T is derived from it. This is the value of the surface tension of the liquid in contact with its own vapour.

Case (1), $r/a_1 < 0.25$. Consider a narrow vertical capillary standing in an open vessel of liquid. The equation $2T(1/b_1 - 1/b_2) = g\rho H$ holds, but, since one tube is infinitely wide, we may neglect $1/b_2$ and write, for the narrow tube, $2T/b = g\rho H$, or

$$a_1^2 = \frac{2T}{g\rho} = bH. \quad (27)$$

This value of a_1^2 is substituted in Rayleigh's formula* for very narrow tubes, namely,

$$a_1^2 = r \left(H + \frac{r}{3} - 0.1288 \frac{r^2}{H} + 0.1312 \frac{r^3}{H^2} \right),$$

the proof of which is too long to give here. Then, by equation (27),

$$\frac{b}{r} = 1 + \frac{r}{3H} - 0.1288 \frac{r^2}{H^2} + 0.1312 \frac{r^3}{H^3},$$

from which b can be calculated. Substituting in (27), we obtain a numerical value of a_1^2 , and hence find T .

Case (3), $r/a_1 > 6$. Consider a wide vertical tube standing in an open vessel of liquid. In this case Rayleigh's formula for very wide tubes is used, namely,

$$\frac{r}{a} - \log_e \frac{a}{H} = 0.8381 + 0.2798 \frac{a}{r} + \frac{1}{2} \log_e \frac{r}{a}, \quad . . . (28)$$

where

$$a = \frac{a_1}{\sqrt{2}} = \sqrt{\frac{T}{g\rho}}.$$

The proof of (28) is also too long to reproduce here.

From experimental values of r and H , a and T can be calculated.

For tubes in which $2.24 < r/a < 4.24$ no exact formula giving the capillary rise seems to have been put forward, but Sugden gives an approximate graphical method of extrapolation for use in this case.

11. Measurement of the Surface Tension of a Liquid Available only in very Small Quantity.

If the volume of liquid available is only about two cubic millimetres, the method of Ferguson and Kennedy† is very suitable, especially as a knowledge of the density of the liquid is not required.

* Rayleigh, *Proc. Roy. Soc., A*, Vol. 92, p. 184 (1915).

† Ferguson and Kennedy, *Proc. Phys. Soc.*, Vol. 14, p. 611 (1932).

Some of the liquid under test is placed in a clean glass capillary tube C , mounted vertically with its open end downwards, as shown in Fig. 15.

at the mouth of the tube, is plane and horizontal. Since the liquid is in equilibrium, the resultant upward force on it is equal to the resultant downward force. Assuming that the angle of contact is ψ , we get

$$\begin{aligned} 2\pi rT \cos \psi &= \text{Weight of liquid} + \text{Thrust on the top} \\ &= g\rho(\pi r^2 h_1 + \pi r^2/n) + g\rho_2 h_2 \pi r^2, \end{aligned}$$

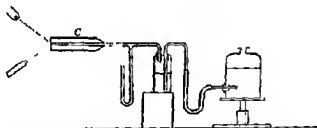


FIG. 15

n being a pure number whose value is 3 when ψ is zero and the meniscus is hemispherical. On reduction, we have

$$\frac{2T \cos \psi}{g} = \rho \left(h_1 + \frac{r}{n} \right) + \rho_2 h_2, \quad (29)$$

meter and is $g\rho_2 h_2$, say, that is, there is a thrust $g\rho_2 h_2 \pi r^2$ acting to the left. There is also a force towards the right of value $2\pi rT \cos \psi$, due to surface tension. For equilibrium we must have

$$2\pi rT \cos \psi = g\rho_2 h_2 \pi r^2, \quad (30)$$

This assumes that the capillary tube is so narrow that the gravitational forces causing a distortion of the right-hand meniscus from the spherical shape are small compared with the forces due to surface tension. In other words, it is assumed that the distortion is negligible.

Comparing equations (29) and (30), we see that

$$\rho_2 h_2 = \rho \left(h_1 + \frac{r}{n} \right) + \rho_2 h_2, \quad (31)$$

Having found, by experiment, that the two sides of this equation are equal, we need only use equation (30) to get

$$T = \frac{\rho \rho_2 h_2 r}{2 \cos \psi} \quad \dots \dots \dots (32)$$

Ferguson and Kennedy show by experiments with liquids for which $\psi = 0$ that equation (31) is satisfied by tubes for which $r < 0.05$ cm. They have also used the method to determine interfacial surface tensions.

12. Pendent Drop at the End of a Tube.

Fig. 16 shows a pendent drop of liquid in equilibrium at the lower end of an open vertical tube. Let there be a column of liquid in the tube above the drop. Let its total height above the bottom of the meniscus be H . This height is usually so great that the effect of the curvature of the meniscus at the top on the pressure at any point in the drop is negligible. Here we shall assume that this is the case.

Consider the equilibrium, as regards vertical forces, of the portion of liquid whose meridional section by a central vertical plane is $OODG$. It is subject to the following forces. Vertically downwards there are the weight mg and a force due to hydrostatic pressure on the plane DC , namely,

$$\pi GC^2 \{P + \rho p(H - OG)\},$$

where P is the atmospheric pressure. Vertically upwards there are the forces $\pi GC^2 P$ due to atmospheric pressure below the drop and $2\pi T GC \cos \theta$ due to surface tension. If we restrict the discussion to cases in which DC is not much above O , we may assume that the profile curve is parabolic and has the equation $y = kx^2$. If the co-ordinates of C are (x, y) , i.e. if $GC = x$, $OG = y$, then the mass of $OODG$, regarded as the sum of the masses of elementary horizontal slices, is

$$\int_0^y \rho \pi x^2 dy = \int_0^y \frac{\rho \pi y}{k} dy = \frac{\rho \pi y^2}{2k},$$

and its effective weight is $\pi \rho g y^2 / 2k$, where $\rho = \rho_2 - \rho_1$.

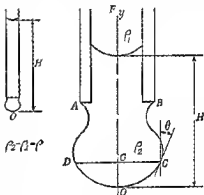
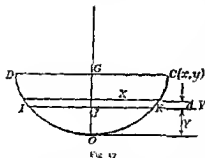


Fig. 16

The equation representing the equilibrium of $CODG$, on which the total downward forces are equal to the total upward forces, is

$$\frac{\pi \rho g y^3}{2k} + \pi x^2 \rho g (H - y) = 2\pi T x \cos \theta. \quad (33)$$



Next, consider the equilibrium, with respect to horizontal forces, of that half of $CODG$ which is convex towards the reader. There is a horizontal force equal to $T \times$ length of arc COD away from the reader. Another horizontal force $T \sin \theta$ per cm. length acts normally to the circumference of the circle whose diameter is DC . This amounts to a resultant $T \times DC \sin \theta = 2xT \sin \theta$ to-

wards the reader. The hydrostatic thrust of the other half of the bottom of the drop, acting towards the reader, is calculated as follows (fig. 17):

Thrust on an elementary strip JK

= pressure at $J \times$ area of strip

= (pressure at O - pressure due to OJ) \times area of strip

= $g\rho(H - Y)2X dY$.

Hence total thrust on section $CGDO = \int_0^y 2g\rho(H - Y)X dY$.

If we put $Y = kX^2$, the integral becomes

$$\begin{aligned} & \int_0^y 2g\rho(H - kX^2)X 2kX dX \\ &= 4g\rho k \left(\frac{Hx^2}{3} - \frac{kx^5}{5} \right), \end{aligned}$$

and if we put $y = kx^2$, this becomes $4g\rho \left(\frac{Hxy}{3} - \frac{xy^2}{5} \right)$ dynes towards the reader

Let the length of the arc COD be l . The horizontal forces on the front half of $CODG$ balance. Hence

$$Tl = 2xT \sin \theta + 4g\rho \left(\frac{Hxy}{3} - \frac{xy^2}{5} \right). \quad (34)$$

On eliminating H from equations (33) and (34), we find that

$$T = \frac{2g\rho xy^2}{15 \left\{ 2x \sin \theta + \frac{8y \cos \theta}{3} - 1 \right\}} \quad \dots \quad (35)$$

Ferguson has applied this formula to the measurement of T . The method is of particular use in measuring T for molten metals.

13. Drop Weight Method of Measuring the Surface Tension of a Liquid. Method of Harkins and Brown.

Instead of a pendent drop, consider a drop of liquid of volume V a.o. which has just ceased to make contact with the lower end of a rod or tube and is falling under gravity. Such a lower end is called a "tip". Let its external radius be r cm. The shape of the drop is complicated, but its weight Mg may be regarded as a function of the surface tension T of the liquid, the radius r of the tip, the volume V of the drop, and other variables. Now the products Mg and Tr have the dimensions of a force. Hence, applying the method of dimensions, we have

$$\begin{aligned} Mg &= Tr \times \text{a non-dimensional function of the various variables,} \\ &= Tr \times f_1(x, y, z, \dots), \text{ say.} \end{aligned}$$

We may take the non-dimensional factor 2π out of the function, leaving

$$Mg = 2\pi Tr f_2(x, y, z, \dots).$$

Since the function must be non-dimensional, we may try the special cases

$$Mg = 2\pi Tr f_3\left(\frac{r}{V^{1/3}}\right) \quad \dots \quad (36)$$

or

$$Mg = 2\pi Tr f_4\left(\frac{r}{a}\right), \text{ where } a^2 = \frac{T}{g\rho}, \text{ the capillary constant.} \quad (37)$$

The constant a has the dimensions of a length.

For any particular drop, $f_3(r/V^{1/3})$ and $f_4(r/a)$ will be numerically equal.

In their researches with water and benzene, Harkins and Brown* weighed the drops of a liquid falling from a given tubular tip. The density was known and hence $V^{1/3}$ was calculated, and thus, from a measured value of r , $r/V^{1/3}$ was obtained. By the capillary rise method, a value of T was obtained experimentally and a value of r/a was calculated. The value of $Mg/2\pi rT$, that is, of $f_3(r/V^{1/3}) = f_4(r/a)$.

* Harkins and Brown, *Journ. Amer. Chem. Soc.*, Vol. 41, Part I, p. 499 (1919).

was then computed. The corresponding values of $f_2(r/a)$ were plotted. The actual determinations of Harkins and Brown dealt with values of r/a ranging from 0.025 to 2.60. The corresponding values of $f_2(r/a)$ did not remain constant, but varied from 0.924 to 0.5352. Precisely the same curves connecting r/a and $f_2(r/a)$ were obtained for four liquids of such varying densities and viscosities as water, benzene, carbon tetrachloride, and ethylene dibromide, that is, the curves were absolutely superposed on one another when plotted on the same sheet of paper. A similar result was found for the curves connecting $r/V^{1/3}$ and $f_2(r/V^{1/3})$. The curves were almost exactly those of a cubic equation.

The unchanging form of the function $f_2(r/a)$ for four dissimilar liquids justifies the belief that from each a curve as the one connecting $r/V^{1/3}$ and $f_2(r/V^{1/3})$, together with a simple drop experiment, the surface tension of any liquid can be found. All that is necessary is to carry out a drop weight experiment with the liquid, measure M and r , and calculate $r/V^{1/3}$; in the tables of Harkins and Brown or on the appropriate graph determine $f_2(r/V^{1/3})$, which is equal to $f_2(r/a)$, and on the other graph find the corresponding value of r/a and calculate a and T .

Practical Details.—The apparatus is placed in a thermostat. If a drop were allowed to form and fall under gravity alone, it would take its full "drop time" of more than three minutes. A large part of it is therefore formed by suction on the part of the operator and it is then allowed to complete its growth and fall under gravity. Usually a thirty-drop run is taken, which requires about 30 min.

Comments.—(1) The equation $Mg = 2\pi rT$, sometimes called Tate's law, is seen to be incorrect.

(2) The ratio of the surface tensions of two liquids is not equal to the ratio of the weights of drops falling from a given tip, as is often assumed.

(3) Any departure from a circular shape of the edge of the tip introduces error. Hence a special method of grinding is used.

(4) The method can also be applied to interfacial surface tensions, indeed,

in that it involves some uncertainty about the angle of contact.

A more accurate expression* for the surface tension when the ring is made of material with a rectangular section, and when $\theta_s = 90^\circ$, is

$$T = \frac{F}{4\pi R} \left[1 - \left\{ 2.8284 + 0.6095 \sqrt{\frac{h}{R}} \right\} \frac{s}{\sqrt{hR}} + \left\{ 3 + 2.585 \sqrt{\frac{h}{R}} + 0.371 \frac{h}{R} \right\} \frac{s^2}{hR} \right],$$

where F is the maximum extra force, R is the mean radius of the ring, $h = \frac{F}{\pi R^2 \rho g}$, $\rho = \rho_1 - \rho_2$, and $2s$ is the thickness of the ring, measured vertically.

15. Measurement of Surface Tension by the Ring Method.

The ring method is particularly useful in studying the progressive changes which occur in the surface tensions of various liquids with the passage of time.

(1) *Lecomte du Nôly's apparatus*† will now be described. A ring of platinum containing 10 per cent of iridium hangs from an inverted Y frame of the same wire, to which it is "sweated". This system can be cleaned by heating. It is suspended from an arm A of a special horizontal torsion balance, called a *tensimeter*. The wire of the ring is of circular section, about 0.3 mm. in diameter, its mean circumference being about 4 cm. The torsion wire is steel piano wire of diameter 0.25 mm. The liquid lies in a clock glass. In the experiment a pointer F attached to the torsion wire rotates over a fixed circular scale as the ring is raised. The beam A is kept horizontal by lowering the support carrying the liquid. The maximum angular reading θ of the pointer is noted. The scale is calibrated in the absence of liquid by attaching known weights to the ring, so that θ corresponds to a certain maximum extra pull P . The ring is of such thin wire that du Nôly assumes that

$$P = 4\pi RT, \quad \dots \dots \dots (40)$$

The method has the following advantages: (1) Only a small quantity of liquid is required. (2) Each reading takes only about 20 sec. (3) The pull is measured to within 0.1 dyne. (4) Comparisons with standard liquids are quickly made.

(2) *The Ring Method of Harkins, Young and Cheng*.‡—Consider a metal ring of circular wire, suspended horizontally in a liquid. As the ring is gradually raised out of the liquid, the extra downward pull on it in addition to the weight passes through a maximum value. If the ring is made of thin wire, the maximum pull is given approximately by $P = 4\pi RT$, where R is the mean radius of the ring and T is the surface tension. If the wire is not thin, the calculation of F , the maximum extra force, is more complicated. Since $4\pi RT/P$ is the value of R/r calculated from the calculation, and R/r is the value of R/r determined by the experiment, they assumed that

$$\frac{4\pi RT}{P} = f_1\left(\frac{R}{r}\right) \quad \dots \dots \dots (41)$$

or

$$\frac{4\pi RT}{P} = f_2\left(\frac{R^3}{V}\right), \quad \dots \dots \dots (42)$$

where V is the volume of liquid held up by the maximum pull of the ring (which is equal to $P/\rho g$, where ρ is the density) and r is the radius of the wire.

* Verschuiffel, *Comm. Leiden, Suppl. No. 42d*, (1918).

† Lecomte du Nôly, *Journ. Gen. Physiol.*, Vol. 1, p. 521 (1919).

‡ Harkins, Young and Cheng, *Science*, Vol. 64, p. 303 (1926).

Using water, benzene and bromobenzene, liquids of known surface tension, they measured the maximum pull on three rings of different R and r but constant R/r . They plotted graphs in which the abscissae were values of R^3/V and the ordinates were values of $4\pi RT/P$. The points for all three liquids were found to lie on one smooth curve. They inferred that if the same rings and other liquids had been used, the values of R^3/V and $4\pi RT/P$ would have given points on the same curve.

To obtain an accurate value of the surface tension of another liquid, the procedure is as follows. Take a ring of the same metal and same R/r as one of those used by Harkins, Young and Cheng. Use it to measure the maximum pull as it is raised out of the given liquid. Calculate $R^3/V = R^3 g g_0/P$. Find the point on the graph of Harkins, Young and Cheng, for rings of the same R/r as that used, which has the abscissa R^3/V . Read off the value of the ordinate y , which is $4\pi RT/P$, and from it calculate T , the surface tension, which is given by $gP/4\pi R$.

The practical precautions employed may be summarized as follows:

- (1) The whole apparatus is enclosed in a thermostat to keep the temperature constant.
- (2) The surface of the liquid is swept by barriers to clean it before an experiment.
- (3) The liquid is covered by an inverted glass funnel to reduce evaporation.
- (4) The thermostat is supported independently of the rest of the apparatus, to prevent agitation of the liquid under test.
- (5) The dish containing the liquid is made wide, to prevent errors due to the curvature of the meniscus.

16. Measurement of the Rate of Spreading of a Substance over the Surface of a Liquid.

The ring method has been applied to measure the rate of spreading of a substance over the surface of a liquid, by Cary and Rideal.* A crystal of a fatty acid, e.g. myristic acid, is brought into contact with the surface of an N/100 solution of hydrochloric acid in water. A film of solution of the myristic acid is formed, which spreads out from the crystal. More acid continues to dissolve and to spread until the strength of the solution forming the film reaches a certain value, when spreading ceases. The direct object of Cary and Rideal's experiment is to compare the surface tension at points on the circumference of a circle at whose centre the crystal touches the liquid, at various instants following contact, with that of the N/100 hydrochloric acid before contact, measured at points on the same circle. From the values of the surface tension thus obtained, the mean strength of the solution at points on the circumference of the circle at various instants can be calculated, and hence the rate of spreading of the molecules of the myristic acid.

In the experiment the actual quantity measured is the force required to detach a horizontal platinum ring from the surface of the liquid, and this force is proportional to the surface tension (see equation (40)).

The apparatus is shown in fig. 19. The platinum ring LM is suspended from one arm of a balance, so as to hang just below the surface of the liquid, which

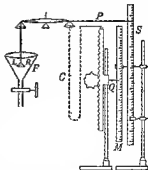


Fig. 19

* Cary and Rideal, *Proc. Roy. Soc., A*, Vol. 109, p. 308 (1925).

is contained in a funnel *F*. The ring is counterpoised by a light eye-glass chain *C*, so supported at one end that weights can be gradually added to that side of the balance. The weight contributed by this chain at any time is known from a previous calibration experiment in which the ring is replaced by weights, and in which a pointer *Q*, attached to the chain, moves over a calibrated scale *M*. The instant when the ring is on the point of being detached is registered by the movement of a long pointer *P* on an arbitrary scale *S*.

The experimental procedure is as follows. Some $N/100$ hydrochloric acid is poured into the carefully cleaned funnel, and the force required to detach the ring is measured. The temperature is then raised to 25°C . and the process repeated.

the zero. The chain is again raised and the process repeated. The temperature of the liquid is recorded.

Results.—Myristic acid and similar substances are found to spread in two stages.

Stage I. The surface is covered by a unimolecular "expanded" film* under zero compression, and if a crystal of constant circumference is used the time required for the spreading is proportional to the area of surface of the hydrochloric acid solution covered. From a crystal of myristic acid of circumference 2.51 mm., used by Cary and Riddal, at 25°C . it was found that 9.06×10^{12} molecules left the crystal per second, i.e. 36.1×10^{12} molecules per sec. per cm. length of crystal face.

Stage II The expanded film of stage I becomes packed more closely with molecules of myristic acid, although it remains unimolecular, that is, one molecule thick. The pressure in the surface increases until there is equilibrium at the surface of the crystal between surface solution and recondensation, that is, until as many molecules return to the crystal per second as leave it.

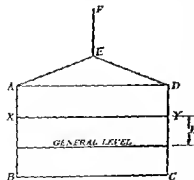


Fig 20

17. Lenard's Frame Method for Surface Tension.†

In this method the experiment consists in the measurement of the maximum pull required to detach a frame *ABCDE* (fig 20) with a cross wire *XY* from the surface of a liquid. In particular, as the frame is being dragged out, a film of liquid attached

* See p. 184.

† Lenard, *Ann. d. Phys.*, Vol. 74, p. 381 (1924).

to the wire XY along its whole length pulls downwards on the frame. It is the maximum value of this pull which is measured.

Regard XY as a horizontal cylinder of length l cm. and radius r cm. Fig. 21 shows a section of the cylinder and film below it. Let the angle of contact be zero, and let θ be the angle made with the horizontal by tangent planes to the liquid and wire at the points of contact K and M . In addition to the weight which the frame has, when XY is dry and just not touching the surface, the downward pull on the frame in the position shown in fig. 20, will be

$$P = 2Tl \sin \theta + hlb\rho - W_1 + W_2, \quad \dots (43)$$

where ρ is the density of the liquid, b is KM in the figure, h is the height of KM above the general level of the liquid, W_1 the weight of the portion KLM of fig.

21 considered as liquid, and W_2 the downward pull due to the removal of the upthrust on the immersed portions of XB and YC which occurs when XY is raised through a height h . The expression $hkb\rho - W_1$ is the weight of the elevated liquid, which pulls downwards on XY . The shape of the surface films

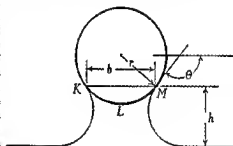


Fig. 21

is cylindrical in the sense of § 3, p. 120, and the theory of that section, and in particular equation (8), applies here. The original form of equation (8) is $g\rho Y^2 = 2T\{1 - \cos(\varphi - \psi)\}$. Now the left-hand side of fig. 21 is comparable with fig. 4. Here $Y = h$, $\psi = 0$, and $\varphi = 180^\circ - \theta$. Hence we have

$$g\rho h^2 = 2T\{1 - \cos(180^\circ - \theta)\} = 2T(1 + \cos \theta) \quad (44)$$

and

$$1 + \cos \theta = \frac{g\rho h^2}{2T} = \frac{h^2}{a_1^2}, \text{ say.}$$

Hence, in the general case,

$$\sin \theta = (1 - \cos^2 \theta)^{\frac{1}{2}} = \left\{ 1 - \left(\frac{h^2}{a_1^2} - 1 \right) \right\}^{\frac{1}{2}}.$$

Also $b/2r = \sin \theta$ and $b = 2r \sin \theta$. If the two vertical wires of the frame each have a radius R cm., $W_2 = 2\pi R^2 g\rho h$. We may now write

$$\begin{aligned} P &= 2Tl \sin \theta + 2klrg\rho \sin \theta - W_1 + 2\pi R^2 g\rho h \\ &= 2l(T + a\rho hr) \left\{ 1 - \left(\frac{h^2}{a_1^2} - 1 \right) \right\}^{\frac{1}{2}} - W_1 + 2\pi R^2 g\rho h. \end{aligned} \quad (45)$$

The position of the first maximum is found as follows.

a is a constant, since the first maximum is very slight. Substitute $h = a_1(1 + x)$, where x is a small quantity compared with unity. Neglect powers of x higher than the first. It is found that the first maximum occurs when

$$h = a_1 \left\{ 1 + \frac{(lr + \pi R^2)}{2l(a_1 + 2r)} \right\} \quad (46)$$

and the corresponding maximum value of the pull * is

$$P_{\max} = 2lT + 2g\rho a_1(lr + \pi R^2) \left\{ 1 + \frac{(lr + \pi R^2)}{2l(a_1 + 2r)} \right\} - \frac{1}{2}\pi r^2 g \rho l \quad (47)$$

In the actual experiment, two series of weighings are carried out. With the

is attached to XY . Other effects, of small importance, near the points X and Y are taken into consideration. In experiments described by Lenard, the length XY varied from 3 to 5 cm., and XY was made of wire of various metals of diameters between 0.03 mm. and 0.1 mm. The frame $ABCD$ was made of wire of diameter from 0.5 mm. to 0.6 mm. In an experiment with earth-nut oil at 21°C ., when XY was made of iron wire, the uncorrected value of T was 3.78 mg./mm. and after correction 3.35 mg./mm. Lenard and his collaborators have improved the frame method until the results are, in their opinion, correct to ± 0.04 per cent. They give the surface tension of water as 72.86 dynes/cm. at 18°C . Lenard asserts that no method in use up to 1924 gave results accurate to ± 1 per cent.

The measurements in the frame method of Lenard are those of length and weight. The measurements in the bubble method are those of pressure and volume.

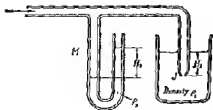


Fig. 22

the whole of the stem of the balance is used. Maximum sensitivity is thus obtained.

18. Determination of the Surface Tension of a Liquid from the Maximum Pressure in Bubbles (often called Jäger's Method).

(1) Elementary Theory.—

A glass jet J (fig. 22), cut off squarely at the tip, is mounted vertically so that the tip is immersed

* Here the approximate value $W = \frac{1}{2}\pi r^2 g \rho l$, corresponding to $\theta = 90^\circ$, which is nearly correct, is used in the last (and small) term.

at a depth H_1 in a liquid whose surface tension is to be found. By means of a dropping funnel, air bubbles are blown at the tip and then break away. A manometer M containing a light liquid of density ρ_2 shows the maximum pressure $g\rho_2 H_2 + P$ in the bubbles before they break away. P is the atmospheric pressure. The elementary theory assumes that the maximum pressure is reached when the bubble reaches a hemispherical shape of radius r equal to the radius of the bore of the jet, and that then the bubble becomes unstable and breaks away. The excess pressure inside the bubble over that outside when on the point of breaking away is assumed to be $2T/r$. This gives the equation

$$\frac{2T}{r} = P + g\rho_2 H_2 - P - g\rho_1 H_1$$

and

$$T = \frac{1}{2}gr\{\rho_2 H_2 - \rho_1 H_1\}. \quad (48)$$

The method is used to measure T at various temperatures. The assumption that instability and detachment occur when the bubble is hemispherical would seem to be unsound. This difficulty is avoided in Sugden's discussion, which we shall now describe.

(ii) *Sugden's Discussion.**—Fig. 23 represents a bubble forming at the end of a jet below the surface of a liquid whose surface tension is required. The figure represents a central section, showing a meridional profile curve.

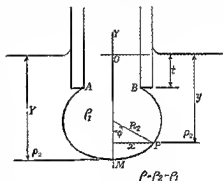


FIG. 23

At a point P on the surface of the bubble, the general equation (4) holds, with a plus sign before gpy , because P is below the general level ($\rho = \rho_2 - \rho_1$). Thus

$$T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + gpy = \text{a constant},$$

if the origin is taken at O in the general level. Alternatively, the same equation may be derived almost from first principles. It expresses the fact that the pressure inside the bubble near P exceeds that outside the bubble near P by $T(1/R_1 + 1/R_2)$. The internal pressure at O

* Sugden, *Journ. Chem. Soc.*, Vol. 121, p. 858 (1922).

is regarded as constant. At M , if each radius of curvature is called b and the depth Y , we get

$$\frac{2T}{b} + g\rho Y = \text{the same constant.} \quad (49)$$

Combining these, we get an equation which holds at any point P :

$$T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + g\rho y = \frac{2T}{b} + g\rho Y.$$

Also

$$\frac{1}{R_2} = \frac{\sin \phi}{x}.$$

Divide throughout by T/b and put $Y - y = z$. Then

$$\frac{1}{R_1/b} + \frac{\sin \phi}{x/b} = 2 + \frac{g\rho}{T/b}.$$

Put

$$\frac{2T}{g\rho} = a_1^2 \quad \text{and} \quad \frac{2b^2}{a_1^2} = \frac{b^2 g\rho}{T} = \beta. \quad (50)$$

Then

$$\frac{1}{R_1/b} + \frac{\sin \phi}{x/b} = 2 + \frac{\beta z}{b}. \quad (51)$$

This equation is the same as equation (23) of § 9, p. 129, and Bashforth and Adams's tables apply to it. They give values of x/b and z/b corresponding to given values of β and ϕ . Sugden applies these tables to the measurement of the surface tension of the liquid in a manner analogous to that which he used in his capillary rise method. His method, in effect, is as follows.

At the point B , t cm. below the general level, $x = r$, the radius of the tube, and

$$\frac{1}{R_1/b} + \frac{\sin \phi}{r/b} = 2 + \frac{\beta z}{b},$$

the ϕ and z now corresponding to the point B , i.e. to $z = Y - t$. The pressure inside the bubble at the level of B is

$$\frac{2T}{b} + g\rho_2 Y - g\rho_1(Y - t) + \text{atmospheric pressure.}$$

The pressure outside at the level of B is

$$g\rho_2 t + \text{atmospheric pressure.}$$

The pressure inside minus the pressure outside, if we put $\rho = \rho_2 - \rho_1$, is

$$\begin{aligned} & \frac{2T}{b} + g\rho(Y - l), \\ &= \frac{2T}{b} + g\rho z, \end{aligned}$$

which can be written in the form $g\rho h$, where h is a positive depth; that is,

$$g\rho h = \frac{2T}{b} + g\rho z$$

or

$$h = \frac{a_1^2}{b} + z.$$

Multiply throughout by τ/a_1^2 ;

$$\begin{aligned} \frac{h\tau}{a_1^2} &= \frac{\tau}{b} + \frac{\tau z}{a_1^2} \\ &= \frac{\tau}{b} + \frac{\tau}{a_1} \frac{z}{b} \frac{b}{a_1} \\ &= \frac{\tau}{b} + \frac{\tau}{a_1} \frac{z}{b} \sqrt{\beta/2}. \quad (52) \end{aligned}$$

Write $h\tau/a_1^2 = \tau/X$, that is,

$$X = \frac{a_1^2}{h}; \quad (53)$$

then

$$\frac{\tau}{X} = \frac{\tau}{b} + \frac{\tau}{a_1} \frac{z}{b} \sqrt{\beta/2}. \quad (54)$$

For a given liquid and orifice, there are fixed values of τ , T , and ρ , i.e. a fixed value of τ/a_1 . If the excess pressure in the bubble alters, so will the shape and size of the latter. For any one pressure there is one value of h , of X , and of τ/X , and corresponding to that value of τ/X there is one value of ϕ , that is, one value of β . Bashforth and Adams's tables give the corresponding values of β , $x/b = \tau/b$, and z/b , and enable τ/X to be calculated by equation (54). Then $T = g\rho a_1^2/2 = g\rho hX/2$.

Calculation reveals that for a given value of τ/a_1 and for steadily increasing values of ϕ , τ/X passes through a maximum which can readily be determined. The reciprocal X/τ passes through a minimum. It is assumed that the bubble breaks away when τ/X has a maximum value, that is, when the excess pressure inside has a maximum value. Sugden gives four-figure tables of minimum values of X/τ and corresponding values of τ/a_1 .

19. Experimental Details of Jäger's Method.

By means of the apparatus in fig. 24 the pressure required to liberate bubbles from the lower ends of two tubes of different radii, immersed to the same depth in a liquid, is measured.

The manometer is used to measure these maximum pressures, which exceed atmospheric pressure by p_1 and p_2 . These excess pressures may be written in the form $p_1 = \rho g H_1$ and $p_2 = \rho g H_2$, where ρ is the density of the liquid under test less that of air.

Let the radii of the tubes be r_1 cm. and r_2 cm.

Then $\rho g H_1$ is equal to pressure due to depth of the lower end of the first tube below the surface + excess pressure of inside over outside at level of the lower end, from fig. 23. Hence

$$\rho g H_1 = \rho g t + \rho g h_1,$$

or

$$H_1 = t + h_1,$$

$$= t + \frac{a_1^2}{X_1} \text{ by (53).} \quad \dots \dots \dots (55)$$

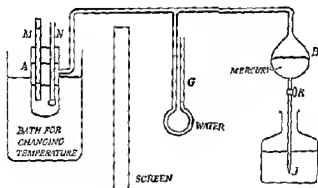


Fig. 24

Similarly,

$$H_2 = t + \frac{a_2^2}{X_2}. \quad \dots \dots \dots (56)$$

Hence

$$H_1 - H_2 = a_2^2 \left(\frac{1}{X_1} - \frac{1}{X_2} \right)$$

or

$$a_2^2 = \frac{(H_1 - H_2)}{\left(\frac{1}{X_1} - \frac{1}{X_2} \right)}. \quad \dots \dots \dots (57)$$

... theory, ... and hence

change from r to $r + dr$, and let the excess pressure change from p to $p + dp$. By the principle of virtual work, the total work done in this change by all the forces keeping the bubble in equilibrium is zero. The work done by the pressure in pushing out the surface = force \times distance = $p \times 4\pi r^2 dr$ ergs, small terms being neglected, and the work done by the surface tension in stretching the surface isothermally is $-Td(4\pi r^2) = -8\pi Tr dr$ ergs. (This assumes the definition of surface tension given on p. 115.) Hence

$$p \times 4\pi r^2 dr - 8\pi Tr dr = 0$$

and

$$p = \frac{2T}{r}. \quad \dots \dots \dots (58)$$

In the case of a soap bubble surrounded by a gas, there are two surface films and

$$p = \frac{4T}{r}. \quad \dots \dots \dots (59)$$

In large bubbles, local pressure differences become more important, the shape is no longer spherical, and the above equations become rougher approximations.

21. Surface Tension of a Liquid found by Measurements on Stationary Drops and Bubbles.

We consider the general appearance of (a) a sessile drop of liquid resting on a horizontal plate, the medium above the drop being a gas; (b) a bubble of gas resting on a plate or projecting from the upper end of a tube, the medium above it being a liquid; (c) a pendent drop of liquid projecting from the lower end of a tube, the medium below it being a gas; (d) a pendent bubble of gas resting under a plate or projecting from the lower end of a tube, the medium below it being a liquid. In all these cases the interface is a surface of revolution about a certain vertical axis, by symmetry.

The accompanying figures, 25 (a), (b), (c) and (d), represent central sections. A and B , O and D are pairs of points close to the surface but on opposite sides of it.

In case (a) the following equations for pressure differences can be written down:

$$p_A - p_s = T(1/R_1 + 1/R_2), \text{ where } R_1 \text{ and } R_2 \text{ are the principal radii of curvature near } A;$$

$$p_o - p_A = -g\rho_2 y, \text{ where } y \text{ is the difference in level of } O \text{ and } A;$$

$$p_o - p_D = 2T/b, \text{ where } b \text{ is the (only) radius of curvature near } O,$$

$$p_s - p_o = g\rho_1 y.$$

Combining these, we get

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2T}{b} + gy(\rho_2 - \rho_1). \quad (60)$$

Case (d) gives the same final equation. Cases (b) and (c) give

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2T}{b} - gy(\rho_2 - \rho_1). \quad (61)$$

These are the differential equations of the meridional curves, that is, profile curves of central sections, and their integrals, if obtainable, would be the equations to these curves. They are not integrable in the general case by rigorous methods. In the special cases of very large drops and bubbles, they are integrable.

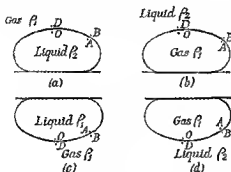


FIG. 25

The theory giving T for large drops and bubbles placed as in (a) and (d) may be stated as follows. Equation (60) reduces to

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = g\rho y, \text{ where } \rho = \rho_2 - \rho_1,$$

since b , the radius of curvature near O , is very great. Further, one of the two radii of curvature near A is very great, since the drop is large, and the equation becomes $T/R = g\rho y$. The theory then proceeds as in § 3, p. 119. Take axes Ox and Oy as shown in fig. 26. Put $R = ds/d\theta$, where θ is the angle made by the tangent at A with Ox , and we have

$$T \frac{d\theta}{ds} = g\rho y.$$

Now

$$\sin \theta = \frac{dy}{ds}.$$

Hence

$$T \sin \theta \frac{d\theta}{dy} = g\rho y,$$

and, multiplying by dy and integrating, we have

$$-T \cos \theta = \frac{1}{2} g\rho y^2 + \text{constant}.$$

When $y = 0$, $\theta = 0$, $\cos \theta = 1$, hence the constant is $-T$. Hence

$$g\rho y^2 = 2T(1 - \cos \theta) \quad . \quad . \quad . \quad (62)$$

is the equation to the meridional curve in terms of y and θ .

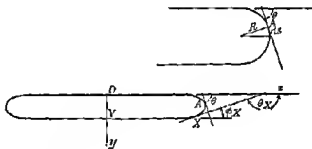


Fig. 26

Put $T/g\rho = a^2$. Since

$$\frac{dy}{dx} = \tan \theta,$$

$$\cos \theta = \frac{1}{\sqrt{1 + \left(\frac{dy}{dx}\right)^2}}$$

and equation (62) can be written in the form

$$y^2 = 2a^2 \left\{ 1 - \frac{1}{\sqrt{1 + \left(\frac{dy}{dx}\right)^2}} \right\}.$$

Hence

$$\frac{1}{\sqrt{1 + \left(\frac{dy}{dx}\right)^2}} = \frac{2a^2 - y^2}{2a^2}.$$

On inverting and squaring, we have

$$1 + \left(\frac{dy}{dx}\right)^2 = \left(\frac{2a^2}{2a^2 - y^2}\right)^2,$$

$$\left(\frac{dy}{dx}\right)^2 = \frac{y^2(4a^2 - y^2)}{(2a^2 - y^2)^2},$$

$$\frac{dy}{dx} = + \frac{y\sqrt{4a^2 - y^2}}{(2a^2 - y^2)}, \quad \dots (63)$$

taking the positive root, since dy/dx is positive when $y^2 < 2a^2$. This may be seen from fig. 26, according to which dy/dx is positive if $\theta < 90^\circ$, and by equation (52), $y^2 < 2a^2$ when $\theta < 90^\circ$.

There are two methods of obtaining a^2 and hence T .

Method (1) arises out of the fact that

$$dy/dx = \infty \text{ when } y^2 = 2a^2 = a_1^2, \text{ say.} \quad \dots (64)$$

This holds for very large or infinite drops. For drops or bubbles which are nearly plane at the vertex, a condition which holds in most practical cases, Ferguson* gives the more accurate formula

$$\frac{dy}{dx} = \infty \text{ when } y^2 = a_1^2 + .606 \frac{a_1^3}{r}, \quad \dots (65)$$

where r is the maximum horizontal radius of the drop.

In the experiment, the values of y and r at the greatest horizontal section are measured with the aid of a microscope, and the value of a_1^2 is obtained by the method of successive approximations.

In one case of a bubble of air in tap water, Ferguson obtained $y = .4061$, $r = 2.540$ cm. by experiment. As a first approximation he put $a_1 = .4051$ in the small second term on the right of the equation $y^2 = a_1^2 + .606 a_1^3/r$ and calculated a better value of a_1^2 in this way.

The value of a_1 derived from this was substituted in the small term, and a new value of a_1^2 was found. The process was repeated until a constant value of a_1^2 was found, namely, $a_1^2 = .1602$, whence T ($= \frac{1}{2}a_1^2 g\rho$) was found to be 73.65 dynes/cm. for tap water at 8°C .

Method (2) arises from the fact that for large drops or bubbles

$$g\rho y^2 = 2T(1 - \cos\theta).$$

At X , $\theta = 180^\circ - \psi$, where ψ is the angle of contact. Let OY , the full height of the bubble, be H . Then

$$g\rho H^2 = 2T(1 + \cos\psi). \quad \dots (66)$$

To obtain the surface tension with the aid of this formula, H must be measured by means of a microscope and ψ must be measured in some special way. Since this method involves a knowledge of ψ , the determination of which always involves a certain amount of doubt, it is not considered as good as the other.

22. Contact of Solids, Liquids, and Gases.

Consider a system (fig. 27) consisting of a solid S and a liquid L . Suppose that they are initially in contact, and are then separated. Let the work per square centimetre required to separate them, that is, the work performed by the operator who separates them, be W_{SL} ergs, say. Before separation there is potential energy in the interface, amounting to T_{SL} ergs per sq. cm., the surface tension of the interface. After separation there is energy T_{SS} ergs per sq. cm. on the surface between the solid and a gas, for example, air, and T_{LG} ergs per sq. cm. on the surface between the liquid and the gas.

The initial energy of the system plus the work of separation which is given to or done on the system is equal to the final energy after separation. Hence we have Dupré's equation

$$T_{SL} + W_{SL} = T_{SS} + T_{LG}. \quad (67)$$

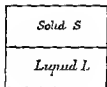


Fig 27

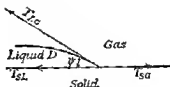


Fig 28

Next consider a system consisting of a liquid, a solid, and a gas all in contact and in equilibrium. Assume that they meet along a common line of contact. The molecules in this line are in equilibrium. Hence, from fig. 28, since the net horizontal forces per centimetre to the left is equal to the net horizontal forces per centimetre to the right,

$$T_{SL} + T_{LG} \cos \psi = T_{SG}. \quad (68)$$

where ψ is the so-called equilibrium angle of contact between liquid and solid. If $T_{SG} - T_{SL}$ is eliminated from equations (67) and (68), we have Young's equation

$$W_{SL} = T_{LG}(1 + \cos \psi) \quad (69)$$

If $\psi = 0$, $W_{SL} = 2T_{LG}$

Now the work required to separate two portions of the same liquid, by reasoning analogous to that at the beginning of this section, is $W_{LL} = 2T_{LG}$ ergs per sq. cm. Hence the meaning of the fact that $\psi = 0$

is that the attraction between solid and liquid is equal to the attraction between two parts of the same liquid.

Extending an idea due to Doss and Rao (1933), Yarnold and Mason (1949) have shown how to give a deeper meaning to equation (68). In their theory they assume that in the case represented by fig. 28, the surface of the solid on the right is partly covered by a film of condensed vapour of the liquid, partly by an adsorbed film of air or other gas, and is partly bare. They discuss two cases in which the liquid is (a) advancing, (b) receding over the solid surface. The full expressions are too long to reproduce here, but if we take the special case when the adsorbed gas or air film is absent, the theory can be quoted.

If, in the case of advancing liquid, σ_1 is the fraction of surface carrying condensed vapour, then a fraction $1 - \sigma_1$ is bare. In equation (68) the energy of 1 sq. cm. of solid-gas interface is not now T_{sg} but is $\sigma_1(T_{sl} + T_{lg}) + (1 - \sigma_1)T_{sg}$. This gives

$$\cos\psi = (1 - \sigma_1)\left(\frac{T_{sg} - T_{sl}}{T_{lg}}\right) + \sigma_1.$$

Similarly, for a receding liquid

$$\cos\psi = (1 - \sigma_2)\left(\frac{T_{sg} - T_{sl}}{T_{lg}}\right) + \sigma_2,$$

where σ_2 is the fraction of surface carrying condensed vapour. In both cases, if there is no condensed vapour film at all,

$$\cos\psi = \frac{T_{sg} - T_{sl}}{T_{lg}}$$

as in equation (68). Hence, according to Yarnold and Mason, the value of ψ given by (68), i.e. the so-called equilibrium angle of contact, is really an upper limit, corresponding to the advance or retreat of the liquid over a completely degassed surface. In both cases, also, if the solid is completely covered by a film of condensed vapour, $\sigma_1 = \sigma_2 = 1$, and $\psi = 0$. In other cases ψ has an intermediate value. Further, in the complete theory, by supposing that an advancing liquid removes air from the solid surface and takes that air into solution, and that the converse occurs with a receding liquid, it has been possible to explain the experimentally found changes in the angle of contact with varying velocities of advance and retreat, and time of immersion.

Effect of Friction.—In practice, when measuring angles of contact, it is necessary, according to Adam and Jessop,* to take into account the friction which

* *Journ. Chem. Soc.*, p. 1865 (1925).

(2) *Angle of Contact between Paraffin Wax and Water. Abiott's Method.**—In this method it is recognized that an angle of contact varies according as the liquid is advancing over the solid, receding, or stationary, and corresponding measurements are made. The effect of varying the speed of the liquid relative to the solid is also investigated.

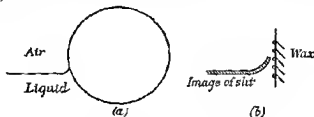


Fig. 31

The main part of the apparatus (fig. 30) is a solid glass cylinder about three inches in diameter and three inches long, which is carefully coated with paraffin wax. After cooling, the surface of the wax is turned smooth. The cylinder is mounted and geared so as to rotate about its own axis, which is horizontal, with various linear surface velocities, up to about 4 mm. per sec. It is partly immersed in water in a special glass tank. One end of the tank is covered with dull black paper, in which a narrow horizontal slit S_1 is made. Parallel light from a lamp passes obliquely upwards through an adjustable slit S_2 , then through S_1 and the liquid, and falls on the under side of the surface of the liquid, whence it is

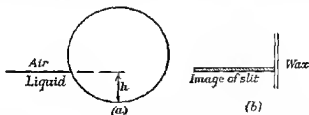


Fig. 32

reflected downwards towards an observer. The observer sees a horizontal image of the slit S_1 adjoining the silhouette of the surface of the cylinder, and that end of the image near the cylinder is in general curved. The depth of the liquid can be altered, but the lamp and S_1 are always arranged so that the point P is in a fixed vertical plane AB . When the cylinder is at rest and the level of the liquid is not specially selected, the general end view of the system, as seen by the unaided eye, is as in fig. 31(a), and when the above optical system is used, the image seen is as in fig. 31(b).

The experiment consists in adjusting the depth of water until the general view is as in fig. 32(a) and the special image as in fig. 32(b). The difference between

* Abiott, *Phil. Mag.*, Vol. 46, p. 244 (1923)

the depth in this position and in that when the liquid just touches the lowest point of the cylinder gives h .

Fig. 33 shows that

$$\cos \phi = \frac{h - r}{r} \quad \dots (73)$$

Ablett's mean value of ϕ is $104^\circ 32'$.

Analogous experiments are carried out with the cylinder rotating in clockwise and anticlockwise directions; in each case the depth is adjusted until a perfect image is seen right up to the line of contact. Ablett found that for surface speeds up to about 0.44 mm./sec. the angles of contact varied in a definite way, but for speeds exceeding 0.44 mm./sec. they became constant. The mean value of ϕ_1 , the angle of contact for anticlockwise rotation, observed on the left-hand side of the cylinder and therefore corresponding to the case of a liquid advancing over a solid, was $112^\circ 58'$. The mean value of ϕ_2 corresponding to liquid receding was $90^\circ 10'$. Within the limits of experimental error $\phi = \frac{1}{2}(\phi_1 + \phi_2)$.

FIG. 33

(3) *Yarnold and Mason's Method*.^{*}—Like Ablett, these authors studied the effect of velocity on the "advancing" and "receding" angles of contact. The range of velocities was less than in Ablett's work, but an interesting novelty was discovered, viz. that the length of the time of previous immersion affected the measured angle of contact.

The experiment consisted in raising or lowering a plane water surface, previously swept clean, at a definite rate while it was in contact with the surface of a steel sphere coated with paraffin wax. The steel sphere was suspended from a Sucksmith ring balance,[†] a sensitive device usually used in magnetism to measure small, continuously applied, variable forces. In this case the Sucksmith ring balance measured the instantaneous downward force X on the steel sphere. Continuous observations were made of this force and of the position of the water surface. The latter quantity enabled y , the height of the centre of the sphere of radius r above the plane liquid surface, to be found.

In general, the sphere was in equilibrium when its downward weight W was equal to the upward resultant force made up of (a) a force U due to displaced liquid, (b) tension X in the suspending fibre, and (c) surface tension acting round the side of the sphere. In the special case when the liquid surface came accurately horizontal right up to the surface of the sphere, the surface tension force, being horizontal, contributed zero to the vertical forces, i.e. force (c) was equal to zero. In this case then, $W = U + X$, and $U = W - X$ and X was given by the Sucksmith balance. Thus U was obtained. Call this special value U_0 . Now the volume of a spherical cap was easily calculated as the integral of the volume of a circular disc and found to be $\pi r^2 \{ (y/r)^2/3 - y/r + \frac{3}{2} \}$ and its ratio to the volume of the whole sphere, $\frac{4}{3}\pi r^3$ was $(y/r)^2/4 - 3(y/r)/4 + \frac{1}{2}$. This was therefore the ratio of U_0 to U , the upthrust when the whole sphere was just immersed.

A graph was plotted in which the abscissae were values of y/r and the ordinates

^{*} Yarnold and Mason, *Proc. Phys. Soc. B*, Vol. 62, p. 125 (1949).

[†] Bates, *Modern Magnetism* (Cambridge University Press, 1951).

al values of U/U_1 . On the same figure $v = y/r$ and ordinates $U_2/U_1 = (y/r)^2/4 -$ point of intersection was noted. Surely the liquid surface came accurately horizontal right up to the surface of the sphere, and at the same time made the obtuse angle of contact ψ with that surface, it followed as in equation (73) and fig. 33 that $\cos \psi = (h - r)/r = -y/r$. Thus ψ was obtained. This method had the advantages (a) that it was not necessary to know or assume the value of the surface tension, and (b) that it did not depend upon a purely visual observation of ψ . The results indicated that the angle of contact decreased with increasing time of immersion, both for advancing and receding liquid. The effect was much more marked in the second case than in the first. In a certain experiment ψ dropped from about 106° to about 87° in 40 minutes for receding liquid, and from 109° to about 105° in 40 minutes for advancing liquid, the fall in ψ being non-linear in each case. In the case of both advancing and receding liquid ψ seemed to approach a limiting value. For constant time of immersion, a slight increase of advancing angle of contact from 108° to 109° was observed as the velocity of advancing liquid increased from 0.2 to 1.6 mm. per min. On the other hand, for a constant time of immersion of 38 min., an increase in velocity of receding liquid from 0.1 to 1.6 mm. per min. was accompanied by a decrease in the angle of contact from 108° to 105° . The results are in good agreement with the view of opinion held by many, since which they

24. Measurement of Interfacial Surface Tensions.

Some of the methods previously described may be used to measure interfacial surface tensions. Mack and Bartell^{*} describe a method of measuring the tension of the surface between water and various organic liquids, which has the advantage of precision and of not requiring more than about 2 c.c. of organic liquid. The case when the liquid is denser than water is discussed here.

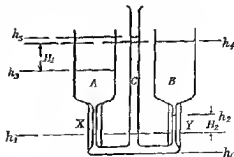


Fig. 34

(From *Jour. Amer. Chem. Soc.* (1932), with slight alterations)

The apparatus, which is made of glass, is shown in fig. 34. It consists of two wide cups A and B, sealed to capillaries X, Y of different radii r_1 , r_2 , and through them joined to a central wide tube C. This arrangement is set up vertically. Water is first poured into A (which is connected to the narrow capillary X) to avoid entrapping bubbles of air. A larger quantity of water is then poured into B. Both capillaries are filled with water and a little extra is added. The organic

* Mack and Bartell, *Journ. Amer. Chem. Soc.*, Vol. 54, p. 936 (1932)

liquid is introduced into the central tube C and rises up the two capillaries. By a certain method of manipulation, the levels are brought near two etched marks on the capillary tubes, and the system is allowed to attain equilibrium. The five different levels are accurately measured. Assume that the interface in X at level h_1 is convex upwards. The vertical cylinder of liquid above the interface is at rest. Hence, equating vertical forces, we have

$$\pi r_1^2 g \left[\left(h_2 - h_1 + \frac{r_1}{3} \right) \rho_0 - \left(h_2 - h_1 + \frac{r_1}{3} \right) \rho_w \right] = 2\pi r_1 T_{12} \quad (74)$$

where ρ_0 , ρ_w are the densities of the organic liquid and of water respectively. Similarly, for the interface in Y ,

$$\pi r_2^2 g \left[\left(h_4 - h_3 + \frac{r_2}{3} \right) \rho_0 - \left(h_4 - h_3 + \frac{r_2}{3} \right) \rho_w \right] = 2\pi r_2 T_{23} \quad (75)$$

Subtracting equation (75) from equation (74), and putting $h_4 - h_3 = H_1$, $h_2 - h_1 = H_2$, $r_2 - r_1 = R$, we find that, if we assume that R is small compared to r_1 or r_2 , and neglect certain terms,

$$T_{23} = \frac{g}{2(1/r_1 - 1/r_2)} \{ (H_1 - H_2) \rho_w + H_2 \rho_0 - \frac{1}{2} R (\rho_0 - \rho_w) \} \quad (76)$$

It is to be noted that in the above equations the approximate expression corresponding to a hemispherical meniscus is used, and r is taken to mean the radius of the capillary in each case. This assumption is justified if we use narrow capillaries. The radius of the larger capillary is less than 1 mm. One advantage of the method is that ρ_0 need not be known more accurately than to two places of decimals, as this quantity only occurs in the small terms of equation (76). One example of a result obtained by Mack and Bartel is that the surface tension of the interface nitrobenzene-water at 15.13° C. is 26.65 dynes/cm.

25. Ripples, and Velocity of Gravity Waves on a Deep Liquid.

One method of measuring the surface tension of a liquid depends on ripples excited upon the surface. Consider the mechanism of a certain type of wave passing over the surface of a deep liquid. In this particular type of wave, the surface of the liquid is traversed by transverse vertical vibrations controlled by the force of gravity. Assume that every drop of liquid in or near the surface describes a circular path in a vertical plane; this is very nearly the actual state of affairs for waves of small amplitude,* as revealed by direct observation.

Fig. 35 represents a section of a liquid traversed by such waves, in a vertical plane parallel to the direction of motion. Let c be the velocity of the waves in a horizontal direction. Assume that every drop of liquid describes a circle of radius r in a clockwise direction. Let τ be the time taken to describe a circle. This is also the time taken by the waves in moving forward through a distance equal to the wavelength λ . As seen by an observer at rest, the motion is *unsteady*, i.e. the velocity of a drop situated at any given point does not remain constant as time passes. If, however, the system is viewed by an ob-

* Ewald, Poschl and Prandtl, *The Physics of Solids and Liquids*, p. 232 (Blackie & Son, Ltd., 1936).

server travelling with the same velocity and direction as the waves, then, as seen by him, the motion is *steady*, and the circular paths of the drops are streamlines to each of which Bernoulli's theorem, that the total energy per gramme is constant along a streamline, applies. We can regard the actual motion of the system, as viewed by an observer at rest, as a combination of a steady streamline motion and a constant velocity c of flow towards the right. In the actual resultant motion each drop describes a circular orbit with velocity $v = 2\pi r/\tau$. Hence in the streamline component motion, although the streamlines are circles, the velocity of a drop is not constant at each point of its circle. At the highest point X of a circle the streamline velocity of a drop is horizontal and is that which, if c is added, becomes

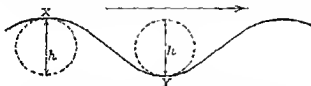


FIG. 25

equal to v , or, alternatively, we can regard it as the velocity of a drop relative to the waves going in the same direction to the right. It is therefore equal to

$$c - c = 2\pi r/\tau - c = q_1, \text{ say.} \quad (77)$$

At the lowest point of the circle whose highest point is X , the streamline velocity is

$$c + c = 2\pi r/\tau + c = q_2, \text{ say.} \quad (78)$$

for this is again the velocity of the drop relative to the waves.

By Torricelli's theorem, which states that the increase in kinetic energy of a drop is due to the fall in height, and hence is equal to the loss of potential energy, we have $q_2^2 = q_1^2 + 2gh$, where $h = 2r$. Hence

$$q_2^2 = q_1^2 + 4gr. \quad (79)$$

By squaring (77) and (78) and subtracting one from the other, we have $q_2^2 - q_1^2 = 8\pi cr/\tau$. Hence $4gr = q_2^2 - q_1^2 = 8\pi cr/\tau$, and $c = g\tau/2\pi = g\lambda/2\pi c$, since $\lambda = c\tau$. Hence

$$c = (g\lambda/2\pi)^{1/2}. \quad (80)$$

26 Effect of Surface Tension on the Velocity of Gravity Waves.

By § 25, the velocity of waves travelling over the surface of a deep liquid and depending only on the force of gravity is $c = \sqrt{g\lambda/2\pi}$.

In order to allow for the effect of surface tension, it is to be noted

that wherever the surface film of a liquid is curved, there is, by § 1, p. 116, a pressure directed from the concave side to the convex side equal to $T(1/R_1 + 1/R_2)$, where T is the surface tension and R_1, R_2 are the principal radii of curvature at the point considered.

Consider simple harmonic waves travelling over a liquid; the position of any point on the surface in a given vertical plane section, parallel to the direction of propagation, at any given moment may be represented by

$$y = a \sin\left(\frac{2\pi x}{\lambda} + b\right),$$

where y is the ordinate of the point above the undisturbed level, λ the wave-length, a the constant amplitude, x the abscissa of the point measured from some arbitrary origin, and b another constant. If we assume that in all sections parallel to the one under consideration

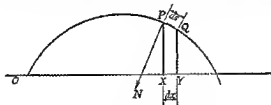


Fig. 36

the profile curve is the same, the system of waves is cylindrical and R_1 , say, is infinite. Also

$$R_2 = \frac{\left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2}}{\frac{d^2y}{dx^2}} = \frac{1}{\frac{d^2y}{dx^2}}$$

if dy/dx is small compared with unity, as is the case in practical experiments on ripples.

If $y = a \sin(2\pi x/\lambda + b)$,

$$\frac{d^2y}{dx^2} = -\frac{4\pi^2 y}{\lambda^2}.$$

Thus at a point such as P in fig. 36 the surface tension causes an excess pressure, directed along NP , of T/R_2 , or along PN of $-T/R_2$, that is, of $4\pi^2 Ty/\lambda^2$ dynes per sq. cm.

The excess force on an element of area whose profile curve is PQ ($= ds$), and whose thickness is 1 cm. measured perpendicularly to the plane of the figure, is $4\pi^2 Ty ds/\lambda^2$ dynes, acting along PN , or $4\pi^2 Ty dx/\lambda^2$ resolved vertically downwards. The principal downward

(restoring) force on the element $PQYX$ is its weight $gpy \, dx$ dynes. The total downward force on it is therefore

$$gpy \, dx + \frac{4\pi^2 T}{\lambda^2} y \, dx \text{ dynes} = yp \, dx \left(g + \frac{4\pi^2 T}{\lambda^2 \rho} \right) \text{ dynes}$$

Thus the effect of surface tension is, as it were, to change g to $g + 4\pi^2 T/\lambda^2 \rho$.

Now the velocity of "gravity waves" on deep liquids has been shown to be $c = \sqrt{\lambda g/2\pi}$.

Hence the velocity of waves controlled by gravity and surface tension is

$$c = \sqrt{\frac{\lambda}{2\pi} \left(g + \frac{4\pi^2 T}{\lambda^2 \rho} \right)}. \quad (81)$$

In this equation we put $c = n\lambda$, where n is the frequency; after squaring, we may rewrite the equation in the form

$$T = \frac{\lambda^3 n^2 \rho}{2\pi} - \frac{g \lambda^2 \rho}{4\pi^2}. \quad (82)$$

It may be easily shown from equation (81) that as λ varies, the velocity c is a minimum when $g = 4\pi^2 T/\lambda^2 \rho$. Hence the least velocity with which water waves can travel is about 23 cm./sec., when λ is about 1.7 cm. These minimum are termed waves, shorts.

If a vertical stick, is inserted into a stream of water whose velocity of flow exceeds 23 cm./sec., stationary ripples are observed in a region upstream from the obstacle. These ripples appear stationary at loci where the forward velocity of the stream is equal to the velocity of backward propagation of the ripples. Since from equation (81) the velocity of the ripples increases when their wave-length decreases, then at points upstream, where the velocity of the water is continually increasing with distance from the obstacle, the effective stationary wave-lengths will become shorter and shorter, and consequently the stationary ripples will crowd ever closer together.

27. Measurement of Surface Tension by the Ripple Method.

This method, introduced by Lord Rayleigh,* has been used by various authors. A recent improvement of the method by Ghosh, Banerji and Datta † possesses several advantages and will now be described.

The liquid whose surface tension is required is placed in a shallow porcelain rectangular trough of dimensions 10 in. \times 6 in. \times 1.5 in. Above the liquid (fig. 37 (a) and (b)) is mounted an electrically-maintained tuning-fork of frequency about 100 vibrations per sec. Its prongs are horizontal, one above the other, when at rest, and they vibrate in a vertical plane. To the lower prong are attached

* *Scientific Papers*, Vol. 3, pp. 383-396.

† Ghosh, Banerji and Datta, *Phil. Mag.*, 7th Series, Vol. 1, p. 1252 (1926).

two objects. First, a blade, 3 in. long, of polished silver or aluminium, called a dipper; this by its up and down vibrations, in and out of the liquid, excites ripples on the surface. The plane of the dipper is vertical, but perpendicular to

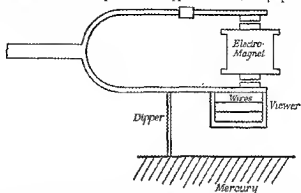


Fig. 37 (a)

the plane of vibration of the prongs. The two trains of ripples excited by the dipper are reflected by the ends of the trough and give rise to stationary ripples. Secondly, a rectangular framework of metal, called the viewer, having two steel wires running horizontally along its length, is attached to the same prong as the dipper, but nearer the tip. The plane of the viewer is vertical, and parallel to the plane of vibration of the prongs. The purpose of the viewer is to enable the wave form of the ripples to be seen and photographed and the wave-length to be measured.

This is done by causing a parallel beam of light, proceeding in planes perpendicular to the plane of vibration of the prongs, to be reflected by the ripple-curved surface of the liquid and to pass obliquely upwards past the wires of the viewer. An observer receiving this light sees that the shadows of the two steel wires are not straight but have the clear wave-like form of the ripples, for the light is proceeding in planes parallel to the crests of the real stationary ripples. A metal plate with two fine notches at a measured distance apart is fixed in the same plane as the wires of the viewer. This is photographed along

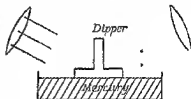


Fig. 37 (b)

with the shadow-ripples and enables the exact wave-length to be calculated from the micrometric measurement of the wave-length of the shadows. It is assumed that the wave-length of the shadows is equal to the wave-length λ of the real ripples on the liquid. The whole device is thus a stroboscopic arrangement for measuring λ , using one fork only. When the amplitude of the ripples is below a certain limit and the depth of liquid in the trough is above a certain limit, the value obtained is constant. The frequency of the fork is determined by the aid of an accurate chronographic recorder tuned in unison with the fork, which also records signals from a standard clock at intervals of one second. The surface tension is calculated from equation (23):

$$T = \frac{\lambda^2 \pi^2 \rho}{2\pi} - \frac{g \lambda^2 \rho}{4\pi^2}$$

where T is the surface tension of the liquid, ρ its density, λ the wave-length of the ripples, and n the frequency of the fork.

28. Stability of a Cylindrical Film.

It is required to show that a circular cylinder of liquid, or a circularly cylindrical film, in equilibrium under the action of surface tension begins to be unstable when the wave-length of a disturbance imposed upon it exceeds the circumference ($\lambda > 2\pi a$).

We neglect the weight, and assume that initially the liquid (fig. 38) is in the form of a circular cylinder of radius a . Let its surface undergo a periodic disturbance such that the radius of the disturbed cylinder at any point A is $y = a + b \cos 2\pi x/\lambda$, where λ is the wave-length. Thus circular symmetry about the axis Ox is assumed. In the disturbed cylinder, equilibrium is stable if the pressure in the swollen parts, e.g.

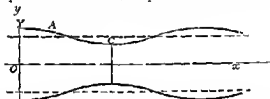


Fig. 38

near Y , is greater than the pressure in the constricted parts, e.g. near O . For then the fluid inside tends to flow back to the constricted parts, thus restoring the initial shape of the film. The excess pressure over the external pressure at any point inside the film is $T(1/R_1 + 1/R_2)$. One of these radii of curvature is y itself (R_1 , say). If we assume that dy/dx is small, then

$$\frac{1}{R_2} = \frac{\frac{d^2 y}{dx^2}}{\left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{\frac{3}{2}}} \approx \frac{d^2 y}{dx^2} \text{ approximately.}$$

Now

$$\begin{aligned} \frac{dy}{dx} &= -\frac{2\pi b}{\lambda} \sin \frac{2\pi x}{\lambda}, \\ \frac{d^2 y}{dx^2} &= -\frac{4\pi^2 b}{\lambda^2} \cos \frac{2\pi x}{\lambda}. \end{aligned}$$

Hence

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{a + b \cos \frac{2\pi x}{\lambda}} \pm \frac{4\pi^2 b}{\lambda^2} \cos \frac{2\pi x}{\lambda}.$$

the positive sign being taken at Y , the negative sign at O . At points such as Y ,

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{a+b} + \frac{4\pi^2 b}{\lambda^2}.$$

At O ,

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{a-b} - \frac{4\pi^2 b}{\lambda^2}.$$

The pressure at Y exceeds that at O by

$$\begin{aligned} & T \left(\frac{1}{a+b} + \frac{4\pi^2 b}{\lambda^2} - \frac{1}{a-b} + \frac{4\pi^2 b}{\lambda^2} \right) \\ &= T \left(\frac{8\pi^2 b}{\lambda^2} - \frac{2b}{a^2 - b^2} \right); \quad \dots \dots \dots (83) \end{aligned}$$

and if $b \ll a$, $a^2 - b^2 = a^2$ approximately, and this reduces to

$$T \frac{2b}{a^2} \left(\frac{4\pi^2 a^2}{\lambda^2} - 1 \right). \quad \dots \dots \dots (84)$$

This is positive, and the cylinder is stable, so long as $4\pi^2 a^2 > \lambda^2$, that is, when $2\pi a > \lambda$. The cylinder ceases to be stable when $2\pi a = \lambda$.

It can be shown that maximum instability occurs when $9.02 a = \lambda$.

29. Jets.

We now attempt to find an expression for the wave-length of a jet of liquid, using the method of dimensions. The symbol S is used here for surface tension to avoid confusion with T , representing time. The study of liquid jets gives useful information about the surface tension of the liquid. When a jet of liquid emerges horizontally from an orifice under pressure, its surface shows peculiar recurrent forms. This phenomenon is partly due to surface tension. Under ordinary conditions the motion of the liquid is "steady" in the hydrodynamical sense, that is, the velocity at any point remains constant and the surface of the jet is fixed in space, though made up of moving drops. The distance between consecutive corresponding points of the recurrent figure may be called the wave-length λ . It is the distance described by the stream during one complete vibration. When the shape of the orifice is given, the wave-length of the jet may be regarded as a function of S the surface tension, ρ the density of the liquid, A the area of the orifice, and P the pressure at which the jet emerges. Viscosity is assumed to play only an unimportant part. The direct analytical determination of λ in terms of S , ρ , A , and P is laborious in the general case, but the method of dimensions gives a certain amount of information about λ .

Assume that $\lambda = \text{a constant} \times S^v \rho^w A^x P^y$, where v , w , x and y are to be found. The dimensions of S are those of force per unit length, i.e.

$$S = MLT^{-2}, L^{-1} = MT^{-1}.$$

Those of ρ are mass per unit volume, hence

$$\rho = ML^{-3};$$

$$A = L^2;$$

$$P = \text{force/area} = MLT^{-2}, L^{-2} = ML^{-1}T^{-2},$$

$$\lambda = \text{constant} \times S^v \rho^w A^x P^y,$$

$$\lambda = (MT^{-2})^v (ML^{-3})^w (L^2)^x (ML^{-1}T^{-2})^y,$$

$$\text{i.e. } L^1 = M^{v+w} L^{-3w+2x-v} T^{-2v-2y},$$

whence

$$v + w + y = 0$$

$$-3w + 2x - y = 1$$

$$-2v - 2y = 0, \text{ on comparing indices.}$$

Solving for w , x and y in terms of v , we get

$$y = -v$$

$$w = 0$$

$$x = \frac{1}{2}(1 - v)$$

and

$$\lambda = \text{constant} \times S^v A^{\frac{1-v}{2}} P^{-v},$$

which may be written in the form

$$\lambda = \text{constant} \times A^{\frac{1}{2}} (SA^{-\frac{1}{2}} P^{-1})^{-v}.$$

Thus v is undetermined.

We may write

$$\lambda = A^{\frac{1}{2}} \times \text{a function of } (SA^{-\frac{1}{2}} P^{-1}) \quad \dots \quad (85)$$

30 Measurement of Surface Tension by means of Jets.

The surface of a jet of liquid emerging from an orifice is being constantly renewed, and hence contamination of the surface due to standing, such as occurs in sessile drops, is absent. This is a considerable advantage from the point of view of accurate measurements of surface tension. Expressions for the surface tension in terms of the wave-length λ of the recurrent form of the jet, the velocity of the jet, and certain constants of the liquid have been calculated by Rayleigh and Bohr for the case where the amplitude of the wave form of the section of the jet is small compared with λ . Rayleigh, Pedersen, Bohr and Stocker have carried out experiments to measure γ , based on these expressions.

* We now revert to the use of γ to represent surface tension.

*Stocker's Method.**—The full expression for the surface tension T of a liquid in the form of a jet emerging in a horizontal direction from an orifice is

$$T = \frac{4\pi^2 c^2 a^3 (\rho_1 + \rho_2) \left\{ 1 + \frac{37}{24} \left(\frac{b}{a} \right)^2 \right\}}{\lambda^2 \left\{ 6 + 10 \left(\frac{\pi a}{\lambda} \right)^2 + 2.5 \left(\frac{\pi a}{\lambda} \right)^4 \right\}} \quad \dots (86)$$

Here c is the velocity of emergence, λ the wave-length, ρ_1 and ρ_2 are the densities of the liquid and of the surrounding air respectively,

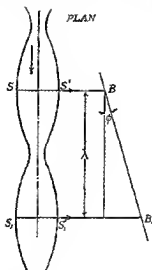


Fig. 30

and the instantaneous radius r at any point is equal to a fixed quantity a plus a fluctuating part whose amplitude is b .

$$\frac{b}{a} = \frac{r_{\max} - r_{\min}}{r_{\max} + r_{\min}},$$

where r_{\max} and r_{\min} are the maximum and minimum radii of the sections of the jet (fig. 39), and

$$a = \frac{1}{2}(r_{\max} + r_{\min}) \left\{ 1 - \frac{1}{6} \left(\frac{b}{a} \right)^2 \right\}.$$

* Stocker, *Zeits. f. phys. Chem.*, Vol. 94, p. 149 (1920).

Stocker's experiments are devoted to the measurement of the various quantities on the right-hand side of equation (30). In his case the liquids are transparent, e.g. water and aqueous solutions, and flow out of an elliptical aperture in the end of a piece of thermometer tubing of elliptical bore. The jet is so arranged that its two perpendicular planes of symmetry are horizontal and vertical respectively. The steady motion is provided by

places. As the jet gets farther from the aperture, internal friction causes its sectional profile to become flatter, S_1S_1' is less than SS' , and the image E_1 is

The velocity c of the jet is obtained by measuring the volume of liquid Q emerging per second and then using the formula $c = Q/\pi r^2$, where r is the mean radius. To obtain Q , an electromagnetic device is arranged so that the jet is permitted to pass through an aperture in a circular disc for a known period of time and is then cut off sharply by the rotation of the disc through part of a revolution. During the time when flow is permitted, the liquid passing is collected; it is then weighed. $Q = W/\rho_1 t$, where W is the mass in grammes collected in t sec., and ρ_1 is the density of the liquid. The greatest and least diameters of the jet, $2r_{\max}$ and $2r_{\min}$, are measured directly by means of a microscope with a micrometer eyepiece, the jet being illuminated over a length of 5 cm. The quantities b/a and c are then calculated, ϵ_1 and ϵ_2 are measured in the usual way.

Result: $T_{1,2} = 72.43 \pm 0.15$ dyne/cm for water

This method is not suitable for an opaque liquid like mercury.

31. Criticism and Comparison of Various Methods of Measuring Surface Tension.

The numerical range of values of surface tension varies from about 10 dynes/cm for some organic liquids to several thousand dynes per centimetre for a liquid metal such as tungsten. A comparison of some

ally carried
contact of the
distance from
the end, and (3) the temperature of the meniscus, are required. It is difficult to measure these quantities with a very high degree of precision. (4) The experiment is static and contamination inside the tube is not improbable. (5) According to Dorsey, the cleaning of a small tube is not easy. (6) A correction for the curvature of the liquid in the reservoir is required. Recent modifications of the original method eliminate some of these difficulties, but not others. Suggden's method, described in § 10, p. 129, eliminates the reservoir correction (6), but

retains (2), (3), (4) and (5), even when the angle of contact may be taken as zero. Ferguson's modification (p. 131) enables the surface tension of a very small quantity of a liquid to be measured with precision.

(ii) *Sessile Drop and Bubble Method*.—Theoretically, this method would seem free from objections, except that the drops have to stand while measurements are being made, and the film runs a certain risk of contamination. In addition, to avoid the introduction of the angle of contact, it is necessary to measure the distance from the plane of maximum diameter to the vertex. Measurements of this quantity appear to involve errors of several per cent (Lenard). To get accurate results it is necessary to carry the approximations rather far. A fair amount of liquid is required. The method is convenient for the determination of the surface tension of molten metals near the melting point.

(iii) *Maximum Bubble Pressure Method (Jäger's Method)*.—This method, as used by Sugden, has the following advantages. (1) It does not involve the angle of contact explicitly, i.e. that angle need not be measured. (2) The internal radius of the tube has only to be measured at the end, where it is easily accessible. (3) Temperature control is good; the bubbles are formed in the middle of a body of liquid of known temperature. (4) Contamination is avoided by continual renewal of the surface involved. (5) A large quantity of liquid is not required.

The theory assumes (1) that static conditions exist, (2) that the internal circumference of the tube on which the bubble forms is circular and horizontal. Dorsey asserts that no attempt has been made to determine how far these conditions may be departed from without introducing appreciable errors.

(4) *Ring Method*.—The ring method has the advantages of rapidity and facility and, as applied by Harkins and his collaborators, great accuracy. It is becoming increasingly important in applied physics.

32. Paper Chromatography.

An elegant application of capillary action was introduced in 1944 by Considen, Gordon and Martin for detecting the presence of the various components of a drop of a mixed liquid solution, such as a protein hydrolysate containing various amino-acids. The method is characterized by the smallness of the quantity of solution used and by the simplicity of the apparatus and procedure.

In the *one-dimensional method*, a rectangular piece of filter paper is touched, at a point not far from one of the shorter edges, by the tip of a micro-pipette containing a drop of the solution under test. The solution soaks into the filter paper forming a small spot and this is allowed to dry. The neighbouring edge of the filter paper is then dipped into a liquid solvent which flows along the paper, through and

past the spot, under capillary action. The various components of the solution in the spot are partially reabsorbed into the solvent, and consequently they travel along the paper, at various rates, behind the sharp line which represents the front of that part of the paper reached by the solvent. A series of new collinear spots are thus formed by the various components of the solution, at the various places they have reached at any given time. The various amino-acids are revealed by spraying the filter paper with a material which stains the spots red, orange, yellow, blue, purple or grey, according to the nature of the amino-acid present.

In the *two-dimensional method* a square sheet of filter paper is used, and after a spot of solution has first been formed and dried near a

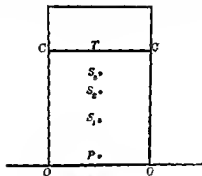


Fig. 40

ment with the colorant, the various coloured spots which correspond to the different components are separated more widely than in the one-dimensional method and therefore the resolution is greater.

As the spots spread, the portion of a solute which remains fixed in the filter paper is termed the *stationary phase* while that which is still spreading with the solvent constitutes the *developing phase*. If a quantity R is defined as the ratio of the distances from the point of origin reached by the front of the developing phase and by the stationary phase respectively, as shown in fig. 40, then it is found that a relation $\alpha = k(R - 1)$ exists. In this expression k is independent of the nature or the concentration of the solute and is therefore constant for a given solvent and filter paper, while α is the *partition coefficient* defined as the ratio of the concentrations of solute in the stationary and the developing phases respectively. The various values of R for the different

spots therefore give the ratios of the corresponding values of α for the different components.

Fig. 40 shows the one-dimensional method of paper chromatography. P is the spot at which a drop of mixture is applied to a vertical filter paper. OO is the line of contact of paper and solvent. S_1 , S_2 , and S_3 are spots reached by different constituents of the mixture. $PS_1 = y_1$, $PS_2 = y_2$, and $PS_3 = y_3$. CTC is the line reached by the developing phase travelling upwards. $PT = y_0$. $R = y_0/y_1$ for the first constituent, $R = y_0/y_2$ for the second constituent, etc.

33. Temperature Relations of Surface Tension.

In considering the way in which the surface tension of a liquid is affected by temperature changes, we must distinguish between "associated" and "unassociated" liquids. An unassociated liquid is one which contains nothing but individual molecules of that liquid, so that if the molecules were further subdivided, the chemical nature of the liquid would be changed. An associated liquid contains groups consisting of individual molecules attached to one another, each group acting like a molecule of another species. There is evidence that at ordinary temperatures water contains groups consisting of two H_2O molecules, in addition to single H_2O molecules. In these circumstances water is an associated liquid. At ordinary temperatures benzene and carbon tetrachloride are unassociated. There is evidence that, as might be expected, the groups of an associated liquid break up as the temperature rises.

The surface tension of unassociated liquids decreases as the temperature rises. The changes may be represented over a wide range of temperature by Ferguson's empirical formula,

$$T = T_0 \left(1 - \frac{\theta}{\theta_c} \right)^n, \quad \dots \dots (87)$$

where T is the surface tension of a liquid in contact with its own vapour, θ the absolute temperature, θ_c the critical temperature of that liquid (in the sense of Andrews*), T_0 a constant, and n a constant for a single liquid, but varying slightly from liquid to liquid. The mean value of n is about 1.2.

Equation (87) is equivalent to one given by Van der Waals. From it we can deduce directly that the surface tension of an unassociated liquid is zero at the critical temperature. By differentiation,

$$\frac{dT}{d\theta} = -\frac{nT_0}{\theta_c} \left(1 - \frac{\theta}{\theta_c} \right)^{n-1} \dots \dots (88)$$

Katayama showed that the relation

$$T\gamma^{-\frac{1}{2}} = A(1 - \theta/\theta_c),$$

* See Roberts, *Heat and Thermodynamics*, fourth edition (1931), p. 107.

where $y = \rho_l - \rho_v$, the difference in the densities of the liquid and of the saturated vapour in equilibrium with the liquid at temperature θ , holds very well for several organic substances. It is also in accordance with the classical theory of corresponding states.

Eötös' Law.—The variation of surface tension of both associated and unassociated liquids with temperature is represented by an equation, due in a simple form to Eötös, but corrected by Ramsay and Shields, namely,

$$T(Mv)^{\frac{1}{2}} = K(\theta_c - \theta - d), \quad \dots \quad (89)$$

where T is the surface tension at θ° absolute; d is a constant term introduced by Ramsay and Shields, which has a value between 6 and 8 for most liquids; θ_c is the critical temperature, x is a number called the *coefficient of association* of the liquid at θ , equal to the effective molecular weight of the associated liquid divided by the molecular weight of an unassociated liquid with the same molecules, and K is a constant which is approximately equal to 2.12 for associated liquids and has a mean value of 2.22 for unassociated liquids, for which, of course, $x = 1$. M is the molecular weight of the unassociated liquid and v its specific volume.

From this law it follows that the surface tension is zero when $\theta = \theta_c - d$, that is, at a temperature a few degrees below the critical temperature. According to Callendar, water has a critical temperature of 653° absolute, but its surface tension vanishes near 647° absolute.

34. Thermodynamics of a Film.

To understand this section some knowledge of thermodynamic formulae and the use of perfect differentials is required.* Let an elementary quantity of heat dH be given to a portion of a film of liquid which has the surface tension T . Some of the energy is used in increasing the internal energy U by dU , and some in performing external work dW . By the first law of thermodynamics,

$$dH = dU + dW.$$

Now the external work dW done by the film as the result of the addition of heat is $-T dA$, where dA is the increase in area. For when a film is stretched by dA , work $+T dA$, which is numerically positive, is done on the film by the operator, that is, $-T dA$ is done by the film. Hence

$$dH = dU - T dA. \quad \dots \quad (90)$$

By the second law of thermodynamics,

$$dH = \theta d\phi. \quad \dots \quad (91)$$

* For a detailed exposition see Roberts, *Heat and Thermodynamics*, Chaps. XII and XIII.

where $d\phi$ is the increase in entropy, if we suppose the heat to have been used up in performing reversible processes only. Now U , θ and ϕ may be regarded as functions of any pair of variables connected with the film which we care to select, and hence $U - \theta\phi = F$, say, is also a function of any pair of variables. Differentiate F . Then

$$dF = dU - \theta d\phi - \phi d\theta = T dA - \phi d\theta. \quad (92)$$

Since dF is a perfect differential of F with respect to A and θ , it follows from equation (92) that

$$\left(\frac{\partial T}{\partial \theta}\right)_{A \text{ const.}} = - \left(\frac{\partial \phi}{\partial A}\right)_{\theta \text{ const.}} \quad (93)$$

Since $d\phi = dH/\theta$,

$$\left(\frac{\partial H}{\partial A}\right)_{\theta \text{ const.}} = -\theta \left(\frac{\partial T}{\partial \theta}\right)_{A \text{ const.}} \quad (94)$$

Physically, this equation means that when a film is stretched isothermally, heat must be added to keep the temperature constant, and this heat, reckoned per unit increase in area, is equal to the product of the absolute temperature and the temperature coefficient of surface tension, with its sign changed. The product, with the sign changed, is numerically positive. Now when the area of a film is increased isothermally by 1 sq. cm., work equal to T ergs is required to perform the stretching, and energy equal to $-\theta(\partial T/\partial \theta)_A$ must be supplied to keep the temperature constant. We may suppose that both these amounts of energy are contained in the new portion of film, 1 sq. cm. in area. The total energy in that 1 sq. cm., as far as surface tension is concerned, is U_1 , say, and is equal to

$$T - \theta \left(\frac{\partial T}{\partial \theta}\right)_{A \text{ const.}} \quad (95)$$

Every square centimetre of a large film may be supposed to be produced by stretching, starting from a film of negligible area. Hence $U_1 = T - \theta(\partial T/\partial \theta)_{A \text{ const.}}$ is the total surface energy per square centimetre of a film of any size. T , the surface tension, is called the "free" or "available" energy and $-\theta(\partial T/\partial \theta)_{A \text{ const.}}$ is called the "bound" energy. In the case of water at 15° C., T is approximately 74 dynes per cm., and $-\theta(\partial T/\partial \theta)_{A \text{ const.}}$ is approximately +43 dynes per cm. The second term is important. (On pp. 117 and 148, we neglected it, thereby assuming that the energy it represents is taken by the film from its surroundings, to maintain a constant temperature.)

When a film, like a soap film in an ordinary soap bubble, has two faces, the total energy has the form

$$U_1 = 2 \left\{ T - \theta \left(\frac{\partial T}{\partial \theta}\right)_{A \text{ const.}} \right\}. \quad (96)$$

35. Relations connecting Surface Tension and Other Quantities.

(1) *Macleod's Relation*.—A large number of non-associated substances, with a wide range of chemical properties, obey the empirical law

$$T = K(\rho_1 - \rho_2)^2 \quad (97)$$

over a wide range of temperature. Here T is the surface tension, K is a constant for a given substance, and ρ_1 , ρ_2 are the densities of a liquid and its saturated vapour at the temperature at which T is measured.

(2) *Sugden's Parachor*.—Even more important than Macleod's relation is that of Sugden, namely,

$$\frac{MT^{\frac{1}{2}}}{\rho_1 - \rho_2} = \text{a constant}, \quad (98)$$

where T , ρ_1 and ρ_2 have their previous meanings and M is the atomic weight of certain elements or the molecular weight of certain molecules or groups of molecules. The constant is called the *parachor* of the particular atom, molecule or group concerned, and is proportional to the molecular volume. The constancy is maintained (1) during temperature variations of a single substance, (2) when the atom, molecule or group concerned is transferred from one compound to another. For example, atomic hydrogen, represented by H , has the same parachor, 17.1, in a large number of compounds. For substances which are saturated in the chemical sense, the parachor is an additive function. Thus, as we proceed along the paraffin series, the parachor of the whole

group CH_2 is added, that is, the parachor of molecular n times the parachor of CH_2 from the parachor of a paraffin with the formula C_nH_{2n+2} , and has the value 34.2. For a large number of compounds it has been found

that the parachor derived from the expression $\frac{MT^{\frac{1}{2}}}{(\rho_1 - \rho_2)}$ can also be

calculated by adding together two sets of constants, one for the parachors of the atoms in the molecule, the other for the constitutional influences of unsaturation and ring closure. Thus constitutional factors such as double bonds, triple bonds, and rings have a definite parachor which is independent of the atoms or groups concerned. For example, a double bond has the same parachor when it exists between C and C, C and O, or N and O. Provided the bonds of a six-membered ring remain constant, the total parachor of the bonds remains constant, even though the identity of the groups changes

36. Molecular and Other Theories of Capillarity.

From time to time attempts have been made to explain capillary phenomena in terms of some fundamental property of matter, e.g. a law of force between particles, without introducing arbitrary *ad hoc* hypotheses. One of the most celebrated is that of Laplace, a brief account of which will be given here.

(I) *Laplace's Theory*.—It is assumed that every particle of matter in the universe attracts every other particle with a force which is some function of the distance apart. The precise value of this force

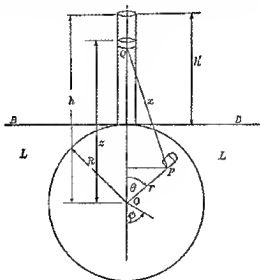


Fig. 41

is not stated, but it is assumed that when the distance apart exceeds a certain limiting value, called the range of molecular action, the value of the force becomes negligibly small and is reckoned as zero.

Attraction of a Sphere on a Cylinder resting on it.—Consider the attraction of a sphere of matter of density ρ on a cylinder of the same matter resting upon its surface as in fig. 41.

Let the cylinder have a cross-section of area 1 sq. cm., and let its height be $(h - R)$ cm. $= h'$. In particular, consider the attraction between an element of matter, of volume $r^2 \sin \theta dr d\theta d\phi$, near the point P , and an element of the vertical cylinder near the point Q . Assume the law of force to be such that particles, each of unit mass, whose distance apart is z cm., exert a force on one another, in the

direction of increasing x , of value $-dV_1(x)/dx$ dynes, or, in other words, that the potential at a point x cm. from unit mass has the value $+V_1(x)$. Let $PQ = x$ cm. and let $OQ = z$ cm. The potential energy of unit mass at Q , due to the element of volume $r^2 \sin \theta dr d\theta d\phi$ near P , is therefore $+V_1(x)\rho r^2 \sin \theta dr d\theta d\phi$. The total potential energy V of unit mass at Q due to the whole sphere is

$$+\rho \int_0^{2\pi} d\phi \int_0^\pi r^2 dr \int_0^\pi V_1(x) \sin \theta d\theta.$$

From the figure, $x^2 = z^2 + r^2 - 2rz \cos \theta$, and hence x is a function of both r and θ . Treating x and r as constants, we have, by differentiation, $x dx = rz \sin \theta d\theta$, and since during the integration with respect to θ , r and z are regarded as constant, we may substitute for $\sin \theta d\theta$ the value $x dx / rz$ and rearrange the expression for V , as follows:

$$V = +\rho \int_0^{2\pi} d\phi \int_0^\pi \frac{r dr}{z} \int_{x-r}^{x+r} V_1(x) x dx. \quad (99)$$

The limits in the last integral are $z+r$ and $z-r$, because x has these values when $\theta = \pi$ and $\theta = 0$ respectively. Further,

$$\int_0^{2\pi} d\phi = 2\pi.$$

Hence

$$V = +2\pi\rho \int_0^\pi \frac{r dr}{z} \int_{x-r}^{x+r} V_1(x) x dx.$$

Let

$$\int_\beta^\infty V_1(x) x dx = V_2(\beta), \quad (100)$$

where β is any lower limit, and let $\int_x^\infty V_1(x) x dx = V_2(x)$. Assume that when x exceeds a certain limiting value c , the potential energy of two molecules or particles due to their proximity vanishes. In symbols, $V_1(x) = 0$ when $x > c$. In this case $V_2(x) = 0$ when $x > c$. Assume that the radius of the sphere is so great that $z+r$ is always greater than c ; $z-r$ is sometimes greater than c , sometimes less than c . Then

$$\int_{z-r}^{z+r} V_1(x) x dx = \int_{z-r}^\infty V_1(x) x dx,$$

since $z+r$ and ∞ are both above the limiting value c . Hence

$$\int_{z-r}^{z+r} V_1(x) x dx = V_2(z-r),$$

by (100), and

$$V = +2\pi\rho \int_0^R \frac{V_2(z-r)r dr}{z}. \quad . \quad . \quad (101)$$

The force on unit mass at Q acting towards O is $+\partial V/\partial z$. The force on an element of the cylinder, of height dz , of cross-section 1 sq. cm., and of mass ρdz is

$$+ \frac{\partial V}{\partial z} \rho dz, \quad . \quad . \quad . \quad (102)$$

acting towards O .

The total force F acting on the whole cylinder of height $h - R$, say, is

$$\begin{aligned} & \int_0^h \frac{\partial V}{\partial z} \rho dz \\ &= +2\pi\rho^2 \int_0^R \int_0^{h-R} \frac{\partial}{\partial z} \left\{ V_2(z-r) \frac{r}{z} \right\} dz dr \\ &= -2\pi\rho^2 \left\{ \int_0^R \frac{V_2(R-r)r dr}{R} - \int_0^R \frac{V_2(h-r)r dr}{h} \right\} \\ &= -2\pi\rho^2 \left\{ \frac{1}{R} \int_0^R V_2(R-r)r dr - \frac{1}{h} \int_0^R V_2(h-r)r dr \right\}. \end{aligned}$$

In the second integral $(h-r)$ occurs. Now $(h-r) \geq (h-R)$. Assume that the cylinder has a finite length $h - R$, which exceeds the range of molecular action c . Then $V_2(h-r) = 0$, because $(h-r) \geq (h-R) > c$, and the second integral is zero. Hence

$$F = -\frac{2\pi\rho^2}{R} \int_0^R V_2(R-r)r dr.$$

Put $R - r = s$.

$$\begin{aligned} F &= \frac{2\pi\rho^2}{R} \int_0^R V_2(s)(R-s)ds \\ &= 2\pi\rho^2 \int_0^R V_2(s)ds - \frac{2\pi\rho^2}{R} \int_0^R V_2(s)s ds, \end{aligned}$$

which may be written

$$F = K - \frac{H}{R} \quad . \quad . \quad . \quad (103)$$

In an analogous manner it may be proved that on a similar internal cylinder the force of attraction is

$$F = K + \frac{H}{R} \quad . \quad . \quad . \quad (104)$$

Comments.—(1) When R is infinite,

$$F = K_{R=\infty} = K_{\infty}, \text{ say.} \quad (105)$$

Hence the expression denoted by K_{∞} is the attractive force per unit area exerted by a body distant ∞ from the surface of the liquid.

With unit area of cross-section, we see that if a large mass of liquid, the surface of which exerts on that on the other side is K_{∞} dynes per sq. cm. Since the whole liquid, or any cylinder of it, is in equilibrium, it may be assumed that a repulsive force exists as well as an attraction, and this repulsion also amounts to K_{∞} dynes per sq. cm. An externally applied pressure acts in addition to these forces. In this connexion, K_{∞} is often called the "intrinsic pressure" of the liquid. K_{∞} has also several other meanings. It is approximately equal to the internal latent heat of evaporation per unit volume of liquid. Further, the term a/v^2 in Van der Waals' equation of state, $(p + a/v^2)(v - b) = R_1\theta$, is also equal* to K_{∞} . K_{∞} is also the "tensile strength" of a liquid, i.e. the force per sq. cm. required to pull apart a column of liquid, free from bubbles and dissolved gases. For liquids at ordinary temperatures, K_{∞} has a very high value. For water $K_{\infty} = 1.03 \times 10^{10}$ dynes per sq. cm. approximately.

(2) Except when $R < a$, $K = K_{\infty}$. Hence when $R > a$ we may regard H/R as the repulsive force introduced by the curvature of the surface, or as the attractive force exerted when the plane-concave lens shaped portion of space L between the sphere and the tangent plane BE is filled with liquid. In § 20, p. 147, it has been shown that from another point of view, namely, the assumption of the existence of a surface film with a surface tension T , the interior of a sphere of liquid may be supposed to possess an excess pressure with respect to its surroundings, equal to $2T/R$. Comparing the two points of view and the expressions derived from them, we see that $2T/R$ is equivalent to H/R , i.e. $T = \frac{1}{2}H$ or

$$T = \pi \rho^2 \int_0^a V_2(s) s ds. \quad (106)$$

(3) If the sphere is composed of a substance of density ρ_2 and the cylinder of density ρ_1 , it is clear that the factor ρ^2 , in the various expressions, must be replaced by $\rho_1\rho_2$. This applies to the case of a liquid in contact with its own vapour.

Calculation of a Lower Limit for the Range of Molecular Action (Young).—By equation (106), the surface tension T may be written as

$$T = \pi \rho^2 \int_0^a V_2(s) s ds, \quad (107)$$

where $s = R - r$, a length.

Although s may have any value between 0 and R , yet if it exceeds a , $V_2(s) = 0$, by an earlier assumption. All the values of s which do not make $V_2(s)$ zero lie between 0 and a , and in this region $s > r$. Hence the expression

$$\pi \rho^2 \int_0^a V_2(s) s ds$$

is always greater than

$$\pi \rho^2 \int_0^R V_2(s) s ds.$$

* See p. 179. (R_1 is the gas constant.)

Hence T is always less than $\pi p^2 \int_0^{\infty} V_2(s) ds$, that is,

$$T < \pi p^2 c \int_0^{\infty} V_2(s) ds,$$

since c is a constant.

Now $2\pi p^2 \int_0^{\infty} V_2(s) ds$ is the K_{∞} of equation (106). Hence

$$T < \frac{1}{2} K_{\infty} c$$

and

$$c > \frac{2T}{K_{\infty}} \quad \dots \dots \dots (108)$$

Hence $2T/K_{\infty}$ is the lower limit of c , and this may be calculated by substituting numerical values of T and K derived from experiment or theory. For water the lower limit works out at about 6×10^{-9} cm.

(4) From equation (105) we see that on every square centimetre of the surface of a fluid with a plane boundary there is a force directed towards the interior along the normal, of value K_{∞} , which can be written in the form

αp^2 , where $\alpha = 2\pi \int_0^{\infty} V_2(s) ds$. This force is due to the

attraction of the rest of the fluid. Now, to an external observer, the fluid is exerting an outward pressure p , say, which is measurable, that is, there must be an externally applied pressure p to keep the fluid in place. This pressure is applied at the boundary. A cylinder of unit area, such as is shown in fig. 42, with one end in the surface and the other in the interior of the fluid, is in equilibrium. On the outer face there is a total force $p + K_{\infty}$ directed inwards. Hence on the inner face the pressure $P = p + K_{\infty}$. This accounts for the term a/v^2 in Van der Waals' equation of state of a fluid,

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\theta,$$

for the K_{∞} of the present section is αp^2 , which can be written as a/v^2 , where v is the specific volume.

(II) *Van der Waals' Theory.*—In Laplace's original theory the precise forms of the functions $V_1(x)$ and $V_2(x)$ are not stated. In an extension of the theory by Van der Waals, it is assumed that

$$V_1(x) = -\frac{Ae^{-x/\lambda}}{x}, \quad \dots \dots \dots (109)$$

where A and λ are constants; λ is called the radius of the sphere of molecular action. Hence in this case

$$\begin{aligned} V_2(x) &= \int_x^{\infty} V_1(x) x dx \quad \dots \dots \dots (110) \\ &= -A\lambda e^{-x/\lambda}. \end{aligned}$$

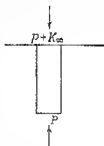


FIG. 42

Also

$$K_s = -2\pi\rho^2 A\lambda^2 \text{ and } H_s = -2\pi\rho^2 A\lambda^3. \quad (111)$$

Some of the points in the theory from which these expressions are deduced are summarized below.

Laplace's theory and other theories are incomplete in various ways. For example, attractive forces between molecules, particles, or volume elements are not the only forces in operation inside a fluid. There are repulsive forces, for example, (a) those which arise when an attempt is made to superpose one particle on another, and (b) those due to the thermal agitation of the molecules. Further, the equilibrium of a fluid is determined by its "free" or "available" energy, not by the total potential energy of the attractive forces. Finally, the density of a fluid is not constant throughout its whole mass.

Van der Waals takes some of these points into consideration. Instead of assuming that the boundary between a liquid and its vapour is merely a geometrical surface, Van der Waals assumes that a transition layer exists, in which the properties of the liquid to those of a vapour pass through a series of intermediate states. The transition layer is of extremely thin

to the expressions in equations (100), (110) and (111), but the full details cannot be given here.

Bakker, in contrast to Van der Waals, assumes the existence of a transition layer between liquid and vapour, in which the density varies continuously according to the isothermal law obtained by making the temperature constant in Van der Waals' well-known equation of state. He then deduces the total energy in the film, &c., in a similar manner to Van der Waals.

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CHAPTER VIII

Surface Films

1. Surface Films of Insoluble Substances.

A surface film of a substance A on a liquid B in which it is insoluble is usually obtained by dissolving a small quantity of A in some volatile solvent C , and then dropping a little of the solution from a pipette on to the surface of B . When the whole of C has evaporated, a surface film of A remains on B . For example, A may be a fatty acid, B water, and C benzene. Four types of such films have been found to exist.

In order to describe the properties of the films, N. K. Adam and other authorities use the concept of *surface pressure*, derived by analogy from the kinetic theory of gases. The films are nearly all only one molecule thick, and each molecule of a film, or assemblage of molecules, moves about in a two-dimensional region, colliding with other molecules and with the boundaries of the surface. The momentum imparted to the boundaries per cm. per second may be regarded as a force per cm. length exerted "outwards" by the film. This is the so-called *surface pressure* of the film. This force per cm. may also be regarded as the difference of the surface tensions of the pure solvent and of the solvent covered by the surface film, and is due to the presence of the film. In symbols, the pressure $P = T_1 - T_2$, where T_1 and T_2 are the respective surface tensions of the two liquids. Further, if the solution changes in strength, $dP = -dT_2$, since T_1 is constant. A method of measuring this force is given later (p. 185).

(i) Gaseous films.

The first of the four types of film to be discussed is the so-called *gaseous film*, in which single molecules of the substance move about independently. In a perfect gaseous film the lateral attractions of the molecules on one another would be zero and in actual practice they are small. The molecules have properties analogous to those of molecules in a rarefied gas or of molecules of a solute in a dilute solution. They exert a pressure by bombardment of the boundaries. The dimensions of the film pressure are those of force per cm., whereas both the pressure of a gas and the osmotic pressure of a solution have the

dimensions of force per sq. cm. The molecules of such a film are prevented from emerging normally from the surface, that is, from evaporation, by the attraction exerted upon them by the molecules of the subjacent liquid; this, however, is not very great, or the film would dissolve. For example, in the case when films of alcohols or fatty acids float on water, this attraction is due to end groups such as OH or COOH, which are termed *hydrophilic*.

It is convenient to exhibit the properties of these films by graphs (fig. 1) in which the abscissa is the pressure in dynes per cm., and the ordinate the product of pressure and area per molecule, the temperature being constant. If the film were perfect, in the sense that a perfect gas is perfect, the product PA would

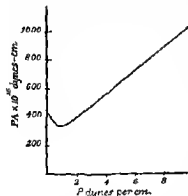


FIG. 1

be constant at constant temperature. In practice, e.g. for films of certain esters of the dibasic acids on water, which approach most nearly to the perfect state, the $PA \sim P$ graph starts, for temperatures near 18°C , and for $P = 0$, at a point where PA is about 400×10^{-16} dynes-cm., which is the value for a perfect gaseous film at that temperature. The graph then descends a little, but soon bends upwards and continues almost as a straight line, like the $PV \sim P$ graph for real gases.

The value of the product PA for a perfect gaseous film may be calculated as follows. By the theorem of equipartition of energy,* we may assign to every molecule of the film a kinetic energy of $\frac{1}{2}k\theta$ ergs per degree of freedom, where k is Boltzmann's constant, 1.372×10^{-16} . If we assign two

degrees of freedom to each molecule, since it can only move in two directions, the kinetic energy per molecule is $1.372 \times 10^{-16} \times 2$ ergs. As in the elementary kinetic theory of gases, but replacing PV by PA , we get $PA = 1.372 \times 10^{16} \times 2$, where A is the area per molecule in sq. cm. At a temperature of 18°C ($=291^\circ \text{K}$), $PA \approx 300.2 \times 10^{-16}$ ergs.

It is probable that in the gaseous films of long-chain molecules, these molecules lie with their longest dimension more or less parallel to the surface. The characteristic features of a gaseous film are that its surface pressure remains continuous down to very low values at very large areas and that the value of the pressure is still given by $PA = k\theta$, when P is very small.

(ii) Condensed or "coherent" films

This type of film, which is much more common than the last, is composed of groups or "islands" of molecules adhering to one another but separated by relatively large areas. Like the gaseous film, this kind of film is only one molecule thick. Individual molecules leave

* See JANAK, *Dynamical Theory of Gases*, sections 99 and 100.

the islands at rare intervals. The surface pressure exerted by the film on the boundaries is due to bombardment by islands, not by individual molecules.

Such films may be demonstrated experimentally by dropping a solution of triolein or oleic acid in a volatile solvent on to the surface of clean water.

On reduction of the surface area, myriads of small islands become visible under the microscope where they exhibit Brownian motion.

Fig. 2 shows two graphs, in which the abscissa is the area per molecule and the ordinate the surface pressure, for two types of condensed

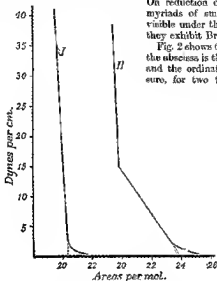


Fig. 2

film. Graph I represents the behaviour of a film of a fatty acid on old distilled water. For most of its length it is a steeply-inclined straight line, with a short rounded part at the lower end due to certain experimental errors. The straight part when produced meets the horizontal axis where $A = 20.5 \times 10^{-16}$ sq. cm. per molecule. It is probable that in such cases the cross-sections of the end groups of the long-chain compounds affect the closeness of the packing. If the end groups have large volumes under low pressures, they will prevent the chains from packing tightly together; but if the end groups are compressible or can be "tucked" away into recesses in the chains of neighbouring molecules, increasing pressure will produce changes in area such as are represented by the less steep part of graph II.

Pursuing the analogy between the behaviour of surface films and that of any working substance undergoing pressure and volume changes, we now see that the condensed films are analogous to liquids. The passage of a condensed film into a gaseous one is analogous to the passage of a working substance from the liquid state to the gaseous state. Such changes take place at very low surface pressures, namely, pressures not greater than 0.3 dyne per cm.

For films of fatty acids on water, the graphs connecting pressure and area show just the same features as Andrews' isothermals for carbon dioxide* below the critical point, namely, an almost vertical straight part corresponding to the condensed film, a horizontal part representing the change of state at constant pressure, and a curved part representing the gaseous state. The curves for myristic and tridecyllic acids are shown in fig. 3.

(iii) Expanded films.

There are two types of film whose properties have no analogy with those of a three-dimensional working substance. Their properties are

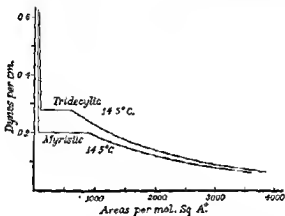


FIG. 3

intermediate between those of the condensed (liquid) and gaseous films. They are called "liquid expanded" and "vapour expanded" films respectively. The characteristic features of the liquid expanded films are that their area per molecule approaches a constant value when the pressure becomes very low, and that they then have a constant surface pressure.

An example of a $P-A$ graph for such a film is shown in fig. 4. LM represents the state at very low pressures. LN represents the film in the liquid expanded state. NOQ represents the gradual change from the liquid expanded to the condensed state. Films of myristic acid on dilute hydrochloric acid show such properties at temperatures near 10°C .

The characteristic feature of vapour expanded films is a gradual expansion, but not to a limiting area or surface pressure. This behaviour

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 106.

is shown by films of ethyl palmitate on a dilute acid. The precise arrangement of the molecules in these films is still unknown.

The type of graph representing the behaviour of a vapour expanded film is shown in fig. 5.

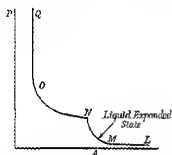


Fig. 4

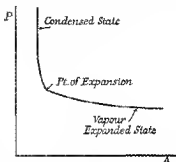


Fig. 5

With some materials, such as some proteins, monomolecular films on an air-water interface cannot be re-expanded if the compression exceeds a certain limit. In the Devaux effect a solid fibrous thread is produced on compression.

2. Measurement of Surface Pressures and Areas.

The most sensitive method used is one devised by Langmuir and improved by Adam. The experiments are conducted with films floating on a liquid contained in a shallow rectangular brass trough (fig. 6). In a certain case the trough measured 60 cm. \times 14 cm. \times 1.8 cm. internally, and the sides were 1 cm. thick and flat on top. The liquid in the trough is cleaned before a film is formed, by

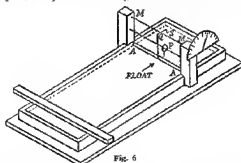


Fig. 6

drawing "barriers", i.e. strips of plate glass, over the liquid surface to "scrape" it. When the liquid is water, the barriers and tops of the edges of the trough are coated with hard paraffin-wax (a substance which does not contaminate water) to prevent the film creeping past the barriers.

The pressure of the film is exerted on a float, i.e. a vertical plane sheet *A.A.* of waxed copper foil, which extends almost the whole width of the trough and dips into the liquid. To block the gaps at each end of the float, thin platinum ribbons about 3 mm. wide, attached to the main framework of the trough but

free at the other end are used. The position of the float is indicated by a scale

dependently above the trough links this torsion wire to the silver wire which

length. Again, this thrust multiplied by the effective length of the "arm" linking the silver tension wire to the torsion wire gives the moment of the thrust about the axis of the torsion wire. When the float is in its equilibrium position under the two forces,

$$mga_1 = Pl a_2$$

where mga_1 is the moment of the forces corresponding to the actual torsion-head deflection ϕ required to keep the float in its equilibrium position, P is the film pressure to be measured, l is the effective length of the float, and a_2 is the arm or perpendicular from the axis of the torsion wire to the line of action of the resultant thrust of the film. The area of the film is the area of the rectangle between the float and the next barrier.

An apparatus of this kind will measure pressures down to 0.01 dynes per cm. After the area is altered by moving a barrier it is necessary to make quick readings in order to avoid contamination, especially at very low surface pressures.

3. Surface Films of Solutions.

The state of concentration of the surface film of a solution is usually different from that of the general body of the liquid. In fact, the concentration in the film is governed by the general law that a mechanical system free to move will reach a state of equilibrium in which the potential energy has a minimum value. In particular, it is the

which has a minimum value
(p. 173), we see that the
the free surface energy.

In a system consisting of two components, e.g. a solvent A and a solute B , the surface film is richer in that component which reduces the free surface energy to a minimum. The general name of adsorption is given to the alteration of concentration of a component in the surface film of a liquid, produced by any cause. The terms positive adsorption and negative adsorption are used to indicate the increase and decrease of concentration of a component.

4. Gibbs's Adsorption Formula.

The quantitative relation connecting surface tension and concentration of solute in the surface film and in the main body of a solution is known as *Gibbs's adsorption formula*. In order to derive it, certain definitions are required.

Consider a system consisting of one solvent and one solute. Let the total volume be v c.c., the absolute temperature θ , the total entropy ϕ c.g.s. units, the surface area A sq. cm., the total internal energy of the solution (including the surface film) U ergs, and the surface tension T (dynes/cm. Let the solution have an osmotic pressure of p dynes/sq. cm. Apply the first and second laws of thermodynamics to this system. Let an elementary quantity of heat dH ergs be given to the system and let it be used in increasing the area of the surface by dA sq. cm., and the volume by dv c.c. By the first law of thermodynamics,

$$dH = dU + p dv - T dA, \quad (1)$$

since $+p dv$ and $-T dA$ represent the contributions to the external work done by the working substance. By the second law, if all the energy is used in performing reversible processes only,

$$dH = \theta d\phi. \quad (2)$$

Hence

$$dU = \theta d\phi - p dv + T dA. \quad (3)$$

We now introduce Φ , the thermodynamic potential at constant temperature and pressure. As is usual in thermodynamics*,

$$\Phi = U - \theta \phi + pv. \quad (4)$$

Differentiation gives

$$d\Phi = dU - \theta d\phi - \phi d\theta + p dv + v dp. \quad . . . (5)$$

and, by (3),

$$d\Phi = -\phi d\theta + T dA + v dp. \quad (6)$$

If the system is kept at constant temperature,

$$d\theta = 0 \text{ and } d\Phi = T dA + v dp.$$

Now $d\Phi$ is a perfect or total differential of Φ with respect to any pair of variables such as A and p ; hence, by the properties of such differentials,

$$\left(\frac{\partial T}{\partial p}\right)_{A \text{ const.}} = \left(\frac{\partial v}{\partial A}\right)_{p \text{ const.}} \quad (7)$$

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 381.

Let the total volume v of solution (represented by $LMNO$ in fig 7) contain n grammes of solute. Draw an arbitrary horizontal plane XY

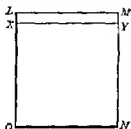


Fig 7

across the liquid very near the top, so as to cut off a portion $LMYX$ of negligible volume compared with $LMNO$. Call the portion $LMYX$, thus defined, the surface film. Let there be m grammes of solute in $LMYX$. We write this in the form $m = Ax$, where A is the area of the surface film perpendicular to the plane of the diagram. Defined in this way, and reckoned in grammes per sq. cm., the quantity x is called the excess concentration in the surface film, and has the dimensions of mass

per unit area. The concentration in grammes per c.c. of the rest of the solution, by the definition of concentration, is

$$\frac{\text{mass}}{\text{volume}} = c, \text{ say,} \\ = \frac{n - Ax}{\text{volume } XYNO} = \frac{n - Ax}{v - \text{vol. } LMYX} = \frac{n - Ax}{v},$$

since $LMYX$ is small compared with v . Hence

$$v = \frac{n - Ax}{c} \quad \dots \quad (8)$$

Substituting from equation (8) in equation (7) and noting that p is constant when c is constant, we find that equation (7) becomes

$$\left(\frac{\partial T}{\partial p}\right)_{A \text{ const.}} = \left(\frac{\partial v}{\partial A}\right)_{p \text{ const.}} = \left(\frac{\partial v}{\partial A}\right)_{c \text{ const.}} = -\left(\frac{x}{c}\right). \quad (9)$$

Assume that the solution is dilute and obeys van't Hoff's law, $p = R_1 \theta c$, where

$$R_1 = \frac{\text{universal gas constant } (R)}{\text{molecular wt. of solute}}$$

Then if θ is constant, $dp = R_1 \theta dc$ and

$$\left(\frac{\partial T}{\partial p}\right)_{A \text{ const.}} = \frac{1}{R_1 \theta} \left(\frac{\partial T}{\partial c}\right)_{A \text{ const.}} \quad \dots \quad (10)$$

Comparing (9) and (10), we get

$$x = -\frac{c}{R_1 \theta} \frac{\partial T}{\partial c} \quad \dots \quad (11)$$

This is the so-called Gibbs's equation in a special form. A more general form of it is

$$x = - \frac{\alpha}{R_1 \theta} \frac{\partial T}{\partial \alpha}, \quad (12)$$

where α is a more general quantity called the "activity" of the solute in the solution (and reduces to c in the special case). The x of equation (12) is the excess concentration in the case of a non-ionized solute.

5. Gibbs's Equation in the case of Ionized Solutes. (Theory of G. N. Lewis.)

In contrast with the last case, we consider a solution in which the solute is ionized. We assume, as is often done, that on the surface of such a solution there is an electric double layer, caused by the positive and negative ions.

In this case the two faces of the surface film are charged with positive and negative electricity respectively, and form, in effect, a charged electrical condenser (fig. 8). The film therefore possesses an additional feature, besides those postulated in the previous section. Let the total charge of each kind of electricity be Q e.s.u., in each case distributed over A sq. cm., and let the potential difference between the faces of the film be V e.s.u. If an elementary quantity of heat dH is given to the film only, an elementary charge $+dQ$ passes across the film from the negative face to the positive. During this process the system has work $+VdQ$ ergs done upon it, that is, it does $-VdQ$ ergs of work. As we are considering phenomena in the film only, the external work done by the osmotic pressure will be ignored in the following equation, which represents the first law of thermodynamics applied to the film:

$$dH = dU - TdA - VdQ. \quad (13)$$

If we assume that no heat is used in performing irreversible processes, the second law of thermodynamics gives

$$dH = \theta d\phi. \quad (14)$$

Hence

$$dU = \theta d\phi + TdA + VdQ. \quad (15)$$

For such a film, the thermodynamic potential at constant electrical potential (instead of pressure) and temperature is

$$\Phi = U - \theta\phi - FQ. \quad (16)$$



Fig. 8

On differentiating and substituting from (15), we have

$$d\Phi = T dA - Q dV, \text{ when } \theta \text{ is constant.}$$

Since $d\Phi$ is a perfect differential,

$$\left(\frac{\partial T}{\partial V}\right)_{A \text{ const.}} = - \left(\frac{\partial Q}{\partial A}\right)_{V \text{ const.}} \quad \dots \quad (17)$$

We now assume that when the charge dQ is carried from one face of the film to the other, it is the net result of the motion of a mass dm_1 grammes of positive ions carrying altogether $+dQ$ e.s.u. in one direction, and of a mass dm_2 grammes of negative ions carrying altogether $-dQ$ e.s.u. in the other. Let the electrochemical equivalents of these ions be ϵ_1 and ϵ_2 respectively. Then, by Faraday's laws of electrolysis,

$$dm_1 = \epsilon_1 dQ \quad \text{and} \quad dQ = \frac{dm_1}{\epsilon_1},$$

$$dm_2 = \epsilon_2 dQ \quad \text{and} \quad dQ = \frac{dm_2}{\epsilon_2}.$$

Substituting these values of dQ in turn in (17), we have

$$\left(\frac{\partial T}{\partial V}\right)_{A \text{ const.}} = - \frac{1}{\epsilon_1} \left(\frac{\partial m_1}{\partial A}\right)_{V \text{ const.}} \quad \dots \quad (18)$$

and

$$\left(\frac{\partial T}{\partial V}\right)_{A \text{ const.}} = - \frac{1}{\epsilon_2} \left(\frac{\partial m_2}{\partial A}\right)_{V \text{ const.}} \quad \dots \quad (19)$$

The expression $\left(\frac{\partial m_1}{\partial A}\right)_{V \text{ const.}}$ is interpreted as the increase in the mass of positive ions per unit increase in area of the film at constant V , that is, as the mass of cations which enters every new square centimetre of area produced by stretching the film; in other words, it is the excess concentration of cations in the film. Similarly $\left(\frac{\partial m_2}{\partial A}\right)_{V \text{ const.}}$ is the excess concentration of anions in the film. The total excess "electrical" concentration is the sum of these,

$$\begin{aligned} &= \left(\frac{\partial m_1}{\partial A}\right)_{V \text{ const.}} + \left(\frac{\partial m_2}{\partial A}\right)_{V \text{ const.}} \\ &= -(\epsilon_1 + \epsilon_2) \left(\frac{\partial T}{\partial V}\right)_{A \text{ const.}}, \quad \dots \quad (20) \end{aligned}$$

an equation which also applies to the electrical double layer at an

interface. The total excess concentration due to non-ionized and ionized solute in a surface or interfacial film is

$$x = -\frac{c}{R_1\theta} \left(\frac{\partial T}{\partial c} \right)_{\theta \text{ const.}} - (e_1 + e_2) \left(\frac{\partial T}{\partial V} \right)_{\theta \text{ const.}} \quad (21)$$

Quantitative experimental tests of this equation have not yet been made.

6. Pressure-Area Relations of Surface Films of Solutions.

(a) *Szyszkowski's relation*.—For certain solutions of those fatty acids which contain from three to six carbon atoms Szyszkowski found an empirical relation, which may be stated thus:

$$P = \alpha \log_{10} \left(1 + \frac{c}{\beta} \right). \quad (22)$$

where P is the surface pressure, α and β are constants for each acid but are different for different acids, and c is the concentration of the liquid in grammes per c.c.

(b) $PA = k\theta$.—We assume that Gibbs's adsorption equation applies to these solutions, which are not ionized. That is,

$$x = -\frac{c}{R_1\theta} \frac{\partial T}{\partial c},$$

by equation (12), where T is the surface tension. As in section 1, p. 181, $dT = -dP$, where P is the surface pressure. Hence

$$x = +\frac{c}{R\theta} \frac{\partial P}{\partial c}, \quad (23)$$

Differentiating Szyszkowski's relation gives

$$\frac{\partial P}{\partial c} = \frac{\text{constant}}{(\beta + c)} = \frac{\delta}{\beta + c}, \text{ say.}$$

Substituting in (23), we have

$$x = \frac{\delta}{R_1\theta} \frac{c}{(\beta + c)} \quad (24)$$

In dilute solutions $\beta \gg c$ and $c/(\beta + c) = c/\beta$, very nearly. Hence $x = c\delta/R_1\theta\beta$ and x/c is constant when θ , the absolute temperature, is constant. Substituting in (23), we find that $\partial P/\partial c = \text{a constant}$ when θ is constant $= K$, say. Hence on integration we have

$$P = Kc,$$

plus a constant which is equal to zero. Now x is the number of grammes per sq. cm. in the surface. Let one gramme contain n molecules. Then nx is the number of molecules per sq. cm. Let A be the area per molecule. Then, since nx molecules occupy 1 sq. cm., $x = 1/An$. Also

$$x = \frac{c}{R_1 \theta} \frac{\partial P}{\partial c} = \frac{c}{R_2 \theta} \frac{P}{c}$$

since

$$\frac{\partial P}{\partial c} = K = \frac{P}{c}.$$

Equating the two values of x , we get

$$\frac{P}{R_1 \theta} = \frac{1}{An},$$

and

$$PA = \frac{R_1 \theta}{n} = k\theta, \quad (25)$$

where $k = \frac{R_1}{n}$ = Boltzmann's constant, 1.372×10^{-16} .

This shows that films of solutions of the shorter fatty acids are "gaseous" in the sense of p. 181. As the length of the molecular chain increases, the behaviour of the films diverges more and more from that of the gaseous films. In some cases, in fact, they first become "expanded" and then "condensed".

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CHAPTER IX

Kinetic Theory of Matter

1. Introduction.

One of the main aims of theoretical physics in the nineteenth century was the reduction of the various branches of physics to mechanics and the ultimate explanation of physical phenomena in terms of Newton's laws of motion. The kinetic theory of matter, and in particular the kinetic theory of gases, affords one of the best and most successful examples of this method of attack. The application of the kinetic theory to liquids is discussed below (see p. 213). In the case of solids, the results can often be better obtained by quantum and thermodynamical considerations.* On the other hand, the classical kinetic theory of gases has suffered comparatively little modification and is therefore discussed here at much greater length.

Since all gases obey, at least approximately, very simple gas laws such as those of Boyle and Charles, it is reasonable to suppose that they all possess a common and simple structure. Basically, the kinetic theory rests on a still more fundamental hypothesis, the atomic theory. The latter dates back to the ancient Greeks and the Roman Lucretius, who maintained that matter is composed of aggregates of hard, indivisible, indestructible, similar parts, termed atoms. The physical implications of the atomic theory were emphasized in the seventeenth century by Gassendi, who suggested that mere motion of the atoms might explain diverse physical phenomena without additional hypotheses. A further advance was made by Bernoulli, who deduced Boyle's law on the assumption that the pressure of a gas arises from impact of the molecules on the wall of the containing vessel. Little development occurred in the following century, but the atomic hypothesis received strong support from chemical theory, particularly from Dalton's laws of the combining powers of the elements. It was not, however, until Joule's classical work on the strict numerical convertibility of mechanical work and heat was carried out in 1848 that the kinetic theory could expand and assume its present comprehensive form.

* See, for example, J. K. Roberts, *Heat and Thermodynamics*, Chap. XXII (Blackie & Son, Ltd., fourth edition, 1951).

The first great advances, due to Clausius in 1857 and succeeding years, were based on the following assumptions, which still form the basis of any elementary treatment of the kinetic theory.

(1) The molecules of a given monatomic gaseous element are regarded as identical solid spheres which move in straight lines until they collide with one another or with the wall of the containing vessel.

(2) The time occupied in collision is negligible and the collision is perfectly elastic.

(3) The molecules are negligible in size compared with the volume of the container.

(4) There are no mutual forces of attraction or repulsion between the molecules.

Clausius also introduced the important conception of the *mean free path* of a gas molecule, which is defined as the average distance traversed by a molecule between successive collisions. The quantities required for a knowledge of the properties and condition of a gas, therefore, are (1) the velocity of the molecules, (2) the value of the mean free path at S.T.P. (standard temperature and pressure), (3) the number of molecules present in unit volume of the gas at S.T.P., (4) the diameter of a gas molecule, regarded as a hard elastic sphere.

This deduction of the gas laws by Clausius and the evaluation of the root mean square velocity of a gas molecule by Joule, some years earlier, were made on the assumption that the velocity of all the molecules in the gas is the same at a given temperature. Maxwell showed later that the velocities were distributed among the molecules according to a probability law. These aspects of the kinetic theory, together with a demonstration of the validity of Avogadro's hypothesis, have already been dealt with in some detail in this series,* and it has been shown that

$$p = \frac{1}{3}\rho C^2, \quad \dots \dots \dots (1)$$

where p is the gas pressure, ρ the density, and C^2 the mean square velocity of the gas molecules.

2. Transport Theorems and the Mean Free Path of a Gas Molecule.

Although Clausius did not succeed in evaluating λ , the mean free path of a gas molecule, ν , the number of molecules per unit volume, or σ , the diameter of a gas molecule, he obtained the useful relation †

$$\lambda = \frac{1}{\pi \sigma^2 \nu}, \quad \dots \dots \dots (2)$$

connecting the three quantities, so that if two of them are known, the third is easily derived. The result was deduced on the basis of a number of over-simplifying assumptions, but it must be emphasized

* See Roberts, *Heat and Thermodynamics*, fourth edition, Chap. III. † *Ibid.*, p. 81

at this stage that the fundamental rule to be observed in the treatment of problems by the kinetic theory is to make the number of simplifying assumptions a maximum. Any reduction in the number of assumptions almost invariably involves enormous complication in the mathematical treatment. In view of present ideas on the electrical structure and wave-like character of atoms and molecules, such detailed treatment is not warranted; the billiard-ball atom is only a crude approximation to reality. The relation obtained by the more accurate treatment usually differs from that obtained by simpler methods only in the introduction of some numerical factor, which, however, may be essential when *quantitative* comparison is made with experiment.

Assuming that all the molecules are in motion with velocities distributed according to a probability law, Maxwell obtained the relation

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi \sigma^2 v} \quad \dots \dots \dots (3)$$

Taking into account also the persistence of velocity on collision, Jeans derives the formula

$$\lambda = \frac{1}{\sqrt{2}} \frac{1.319}{\pi \sigma^2 v} \quad \dots \dots \dots (4)$$

Finally, if intramolecular forces are also considered, the formula of Sutherland* may be obtained:

$$\lambda = \frac{1.402}{\sqrt{2} \pi \sigma^2 v (1 + A/T)} \quad \dots \dots \dots (5)$$

where A is a constant varying with the nature of the gas and T the absolute temperature.

(i) *Transport theorems: general case.*

Consider a volume of gas, one part of which has some property (such as temperature) whose value differs from the value of that property in another region of the gas. Owing to the kinetic velocities, molecules will be continually passing from one region to the other, and a transport of the particular property will therefore be continually taking place. In order to determine the amount of the property transported across unit area in the gas, the number of molecules passing in any particular direction in unit time is required. The simplest method of averaging this number, known as Joule's classification, is to consider a cube situated in the gas. If the area of a face of the cube is dS and v is the number of molecules present in unit volume, then, since there are no preferred directions, at any instant one-sixth of the total number of molecules in the volume will be travelling towards any one of the six sides of the cube.

* Sutherland, *Phil. Mag.*, Vol. 36, p. 507 (1893).

If \bar{c} is the mean velocity of the molecules, the number passing in one direction across the area dS in unit time will be

$$n_1 = dS \frac{\bar{c}}{6} \quad \dots \dots \dots (6)$$

Now on the average, the last collision a molecule makes before crossing the area dS (normal to the x -axis) will have occurred at the mean

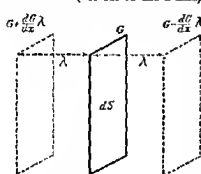


FIG. 2

free path λ from dS . Hence if G represents any property which is being transported across the area (fig. 1) and G is its particular value at the plane dS , the molecules which pass in one direction will have, on the average, a value of G given by $\left(G + \frac{dG}{dx} \lambda\right)$, and those which pass in the reverse direction will have a value of G given by $\left(G - \frac{dG}{dx} \lambda\right)$. The

property is assumed to have

a uniform gradient over the short distance λ . The net amount of the property transported in unit time is therefore

$$\begin{aligned} \Delta G &= \frac{1}{2} \bar{c} dS \left(G + \frac{dG}{dx} \lambda - G + \frac{dG}{dx} \lambda \right) \\ &= \frac{1}{2} \bar{c} dS \lambda \frac{dG}{dx} \quad \dots \dots \dots (7) \end{aligned}$$

(ii) Coefficient of viscosity.

Maxwell applied equation (7) to evaluate the coefficient of viscosity of a gas in terms of the kinetic theory, and was able to deduce a value for λ , the mean free path. Consider a gas flowing over a surface at rest. Denote the drift velocity of any layer parallel to the surface at a distance x by u (fig. 2). Then owing to the presence of viscosity the drift velocity

layer

The

molecules from below, however, will transport a drift momentum less than mu , while those from above will transport a drift momentum greater than this value. A change in momentum is therefore continually taking place across the area, and by Newton's second law of

motion this gives rise to the viscous force acting along the layer. Here the property G being transported is the momentum mv . Hence, applying equation (7), we have

$$\Delta G = \frac{1}{3} \bar{v} dS \lambda m \frac{du}{dx} = F, \quad \dots \dots (8)$$

where F represents the viscous force acting across the area dS . Now Newton's law of viscosity may be written

$$F = \eta dS \frac{du}{dx} \quad \dots \dots (9)$$

where F is the viscous force across an area dS perpendicular to which there is a velocity gradient du/dx , and η is the coefficient of viscosity. Hence from equations (8) and (9)

$$\eta = \frac{1}{3} \bar{v} m \lambda, \quad \dots \dots (10)$$

or, since $m\bar{v} = \rho$, the density of the gas,

$$\eta = \frac{1}{3} \rho \bar{c} \lambda \quad \dots \dots (11)$$

A much more detailed treatment by Chapman* gives the relation $\eta = \frac{1}{2.64} \rho \bar{c} \lambda$; the treatment by the elementary theory is therefore a very satisfactory approximation.

Experimental determination of η and ρ and the evaluation of \bar{c} in terms of G , the root mean square velocity (see Ex. 4, p. 316), which in turn is given by equation (1), therefore affords a measure of the mean free path λ . In this way Maxwell showed that for hydrogen at N.T.P. $\lambda = 1.85 \times 10^{-8}$ cm.

Examination of equation (11) shows that η should be independent of the density of the gas, since as ρ increases with pressure λ decreases, as is shown by equation (2). This important and unexpected result obtained by Maxwell afforded great support for the kinetic theory of gases. Maxwell demonstrated the independence experimentally with the oscillating disc (see Chapter XII, § 11, p. 284) and showed that over a wide range the rate of damping is independent of the pressure. The relation fails at high and low pressures; the reasons for the failure are discussed later (p. 201). The relation has been retested more recently by Gilchrist, using the concentric cylinder method; the

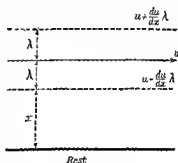


Fig. 2

* Chapman, *Proc. Roy. Soc., A*, Vol. 93, p. 1 (1916).

As with viscosity, the coefficient of thermal conductivity is found to be independent of the pressure, over a moderate range, and to increase approximately as the square root of the absolute temperature, in agreement with equation (16).

(iv) *Coefficient of diffusion.*

An expression for the coefficient of self-diffusion of a gas when different parts of it are at different densities may be obtained from the transport theorem as follows. The property being transported is simply the molecules themselves. Hence if ν represents the number of molecules per unit volume in the immediate neighbourhood of the layer dS , the numbers of molecules per unit volume at a distance equal to the mean free path on either side of dS will be $\left(\nu + \frac{d\nu}{dx} \lambda\right)$ and $\left(\nu - \frac{d\nu}{dx} \lambda\right)$ respectively. Hence, if we apply Joule's classification (p. 195), the net number Δn of molecules transported across dS in unit time is

$$\Delta n = \frac{1}{3} \lambda \bar{c} \frac{d\nu}{dx} dS. \quad \dots \dots \dots (17)$$

Now the basic law of diffusion, due to Fick, is

$$\Delta n = D \frac{d\nu}{dx} dS, \quad \dots \dots \dots (18)$$

where D is the coefficient of diffusion and $\frac{d\nu}{dx}$ represents the density gradient across dS . Hence from (17) and (18) we have

$$D = \frac{1}{3} \lambda \bar{c}. \quad \dots \dots \dots (19)$$

Equation (19) may be written generally in the form

$$D_{12} = \frac{1}{3} \frac{(\nu_1 \lambda_1 \bar{c}_1 + \nu_2 \lambda_2 \bar{c}_2)}{\nu_1 + \nu_2}, \quad \dots \dots \dots (19a)$$

where D_{12} refers to the coefficient of inter-diffusion of two gases, whose numbers of molecules per unit volume and mean free paths are represented by $\nu_1, \nu_2, \lambda_1, \lambda_2$ respectively.

The method commonly used to determine the coefficient of diffusion of two gases is that introduced by Loschmidt, in which a long vertical glass cylinder is separated into two parts by a sliding horizontal diaphragm in the centre. The denser gas is placed in the lower half, the lighter gas in the upper half, and the diaphragm is then removed. After a known interval of time the diaphragm is replaced and the mixtures of gases are analysed, either chemically or by means of some physical property (e.g. the refractive index).

An alternative method, introduced by Stefan, is to determine the change in composition of the gas contained in a vertical jar, the top of which is left open to the atmosphere for a stated period. An extension of this method enables the rate of diffusion of a saturated vapour in contact with its liquid to be determined

by observation of the rate of evaporation of the liquid when the latter is contained in a narrow vertical tube. The tube and liquid are maintained at a constant temperature, a current of gas is sent across the open top of the tube, and the rate of fall of the level of the liquid in the tube is observed. The method is limited to liquids and is practicable over a small temperature range only.

The experimental results for $H_2 - O_2$, $H_2 - N_2$, $N_2 - O_2$, $H_2 - CO_2$, and $He - A$ show that the variation of D_{23} with the composition of the mixture is very much less than that predicted by equation (19a); various corrections to the simple formula, arising e.g. from consideration of the persistence of molecules

coef

physical characteristics, such as thermal conductivity. In the experiments of Harteck and Schmidt,[†] para-hydrogen and ordinary hydrogen were contained in two vessels, each about a metre long and separated by a tap. The tap was opened for about ten minutes, and the composition of the mixture was then determined from the value of the thermal conductivity, using an electrically-heated resistance inserted in the gas and the usual Wheatstone bridge arrangement, as in the Pirani gauge (see § 7 (c), p. 231).

According to equation (19), the coefficient of diffusion should be inversely proportional to the pressure, a result which is confirmed by experiment. Since ρ is inversely proportional to T and \bar{c} is proportional to $T^{1/2}$, the simple theory indicates that $D \propto T^{3/2}$. Experiment shows that $D \propto T^s$, where s lies between 1.75 and 2.0; a satisfactory explanation has been given by Sutherland on plausible grounds based on the kinetic theory.

It will be observed that by equations (11) and (16) $\kappa = \eta C_v$; also, from equations (11) and (19), $D = \eta/\rho$. More rigorous averaging gives $\kappa = e\eta C_v$ and $D = f\eta/\rho$, where e and f are constants, each equal to about 1.4. Experiment shows that while the value for f is in approximate agreement with theory, e is nearer 2.5. The value of the kinetic theory in its simple form, however, is rather in the general correlation which it establishes between diverse properties, such as thermal conductivity, viscosity, and diffusion, and the predictions.

3. Properties of Gases at Low and Intermediate Pressures.

The application of the kinetic theory to predict the properties of gases at low pressures is of great importance, since the results obtained form the basis for the design and operation of pumps and gauges for the production and measurement of high vacua. (An account of these

* See Jeans, *Dynamical Theory of Gases*, Chapter XIII, p. 334 (C.U.P. (1916)).

† *Zeit. f. phys. Chem.*, Vol. 21, B, p. 447 (1933).

is given in §§ 6 and 7, p. 221.) As the gas pressure is reduced, the mean free path increases, until at intermediate pressures it becomes comparable with the linear dimensions d of the containing vessel and at low pressures it becomes much greater than d . At low pressures, therefore, comparatively few collisions occur between the gas molecules themselves, and collisions with the walls of the container become the governing factor.

(i) *Viscous forces at very low pressures.*

Consider two parallel surfaces, of which one is at rest and the other moving in a parallel direction with velocity u_0 . All the molecules which strike the moving surface and then move in the direction of the fixed surface ultimately reach it without further collision, since $\lambda \gg d$. It may be shown* that the number of molecules coming from all directions and hitting unit area of a surface in unit time is given by

$$n = \frac{1}{4} \bar{c} \bar{n}. \quad \dots \dots \dots (20)$$

Now all the molecules will communicate different amounts of sideways momentum to the fixed surface, according to the precise nature of the interaction between the gas molecule and the molecules of the solid. For theoretical purposes, however, it is permissible to define a fraction f , termed the *accommodation coefficient*, such that the fraction is considered to communicate its entire sideways momentum, the remaining fraction $(1 - f)$ being considered to be specularly reflected and to rebound with no transfer of sideways momentum. The sideways momentum transferred per second to unit area of the surface at rest is therefore

$$F = \frac{1}{4} \bar{c} f m u_0 \bar{n} = \frac{1}{4} \rho \bar{c} u_0 f. \quad \dots \dots \dots (21)$$

Now from Ex. 5, Chap. IX, p. 316,

$$\rho \bar{c} = 4p \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}}, \quad \dots \dots \dots (22)$$

where M is the molecular weight of the gas. Hence

$$F = u_0 p f \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}}. \quad \dots \dots \dots (23)$$

Equation (23) shows that at very low pressures the viscous force is proportional to $M^{\frac{1}{2}}$, $T^{-\frac{1}{2}}$, and the pressure p . These predictions contrast strongly with the laws for moderate pressures, where the viscous force has been shown to be independent of p and to vary approximately as $T^{\frac{1}{2}}$. The value of the accommodation coefficient depends on the nature of the gas and the solid, but is usually about 0.8.

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 69.

(ii) *Viscous forces at intermediate pressures*

We again consider two parallel surfaces, one of which is at rest and the other moving with velocity u_0 . Referring to fig. 3, we find that at intermediate pressures the gas may be divided as regards its behaviour into two regions. From the fixed surface outwards up to a distance equal to the mean free path the laws obeyed will be those for a gas at very low pressures, since from anywhere in this region the molecules reach the plate without collision. The effect produced on the plate by molecules with drift velocity in this region is said to give rise to "external" friction. At distances greater than the mean free path from the fixed surface, the laws obeyed will be those deduced for gases at ordinary pressures, since the molecules in this region will

collide frequently with one another and will not, in general, reach the fixed plate immediately after a collision. The viscous forces produced in the main bulk of the gas are said to give rise to "internal" friction. "External" friction is again operative for distances up to the mean free path from the moving plate.

If the velocity of the layer at a distance λ from the surface at rest is denoted by u_1 , "external" friction is operative for velocities

from 0 to u_1 and u_0 to $(u_0 - u_1)$. If the distance between the plates is d , the velocity gradient across the interior of the gas is therefore

$$\frac{du}{dx} = \frac{u_0 - 2u_1}{d - 2\lambda} \quad \dots \dots \dots (24)$$

To evaluate u_1 , the internal and external viscosity coefficients may be equated for the layer at a distance λ from the surface at rest. Now

$$F_{\text{int}} = \frac{1}{2} \bar{v} m \bar{c} \lambda \frac{du}{dx} \quad \dots \dots \dots (25)$$

and if it is assumed that the molecules impinging on the surface at rest have on the average the property of those at a distance λ from it,

$$F_{\text{ext}} = \frac{1}{2} \bar{v} f m u_1 \quad \dots \dots \dots (26)$$

where f is the accommodation coefficient for the molecules colliding with the fixed surface. It should be observed that in equation (26) Joule's classification $\frac{1}{2} \bar{v} \bar{c}$ is used instead of the value $\frac{1}{2} \bar{v}$. The latter is derived

on the basis of all possible free paths and hence cannot be used in an elementary discussion in which the molecules are all assumed to possess the property of those at a distance equal to the mean free path. Hence from equations (25) and (26)

$$u_1 = \frac{2\lambda}{f} \frac{du}{dx}$$

or the velocity gradient near the plate is

$$\frac{u_1}{\lambda} = \frac{2}{f} \frac{du}{dx} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and is approximately twice that in the interior of the gas. The molecules are therefore considered to have, at intermediate pressures, a velocity of slip over the fixed surface equal to

$$v_s = \frac{u_1 + 0}{2} = \frac{\lambda}{f} \frac{du}{dx} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Now from equations (24) and (27),

$$\frac{du}{dx} = \frac{u_0}{d + 2\lambda(2-f)/f} = \frac{u_0}{d + 2\xi} \quad . \quad . \quad . \quad (29)$$

where $\xi = \lambda(2-f)/f$, and is termed the *coefficient of slip*. The effect of lowering the pressure, therefore, has been to increase the distance d at either boundary by an amount approximately equal to the mean free path. The coefficient of viscosity is therefore reduced in the ratio

$$\eta = \frac{\eta_c}{1 + 2\xi/d} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where η_c is the constant value of η at moderate pressures. The viscous force per unit area therefore becomes

$$F = \frac{1}{2} \rho \bar{c} \lambda \frac{u_0}{d + 2\lambda(2-f)/f} \quad . \quad . \quad . \quad . \quad (31)$$

At moderate pressures, where $d \gg \lambda$, equation (31) reduces to the form already given in equation (11). Conversely, at very low pressures, where $d \ll \lambda$, equation (31) reduces to the form

$$F = \frac{1}{2} \rho \bar{c} \frac{u_0 f}{(2-f)} \quad . \quad . \quad . \quad . \quad (32)$$

which agrees with equation (31), except for a numerical factor and the way in which f is involved.

(iii) *Diffusion of gases through an aperture at low pressures.*

If a partition with a small aperture separates two regions in which the numbers of molecules of the gas per unit volume are v_1 and v_2 respectively, there will be a net flow of n molecules per second from one side to the other, where

$$n = \frac{1}{2} A (v_1 - v_2) \bar{c}, \quad \dots \dots \dots (33)$$

A being the area of the aperture, and the whole being at a constant and uniform temperature corresponding to a mean velocity \bar{c} . By (22),

$$\bar{c} = 4 \left(\frac{RT}{2\pi M} \right)^{\frac{1}{2}}.$$

Hence

$$n = A (v_1 - v_2) \left(\frac{RT}{2\pi M} \right)^{\frac{1}{2}}.$$

Since

$$mv = p = \frac{Mp}{RT},$$

we have

$$Q = nm = \frac{A}{\sqrt{2\pi}} (p_1 - p_2) \left(\frac{M}{RT} \right)^{\frac{1}{2}}, \quad \dots \dots (34)$$

where Q is the mass of gas flowing through the aperture per second.

The above formula has been verified by Knudsen,* using platinum partitions having small holes 5×10^{-2} sq. mm. and 6×10^{-2} sq. mm. in area and $\frac{1}{1000}$ mm. thick respectively. The work has been ex-

(iv) *Flow of gas through a tube at low pressure.*

If the mean
transferred to t

$$F = \frac{1}{2} \bar{c} \times 2\pi a l m v_0 f. \quad \dots \dots \dots (35)$$

When a steady flow is in progress, this force must be equal to the force due to the pressure difference acting over the two ends of the tube. Hence

$$\pi a^2 (p_1 - p_2) = \frac{1}{2} \pi a l p_0 \bar{c} v_0 f.$$

and the mean velocity of drift is given by

$$v_0 = \frac{2a(p_1 - p_2)}{l p_0 f}. \quad \dots \dots \dots (36)$$

* Knudsen, *Ann. d. Physik*, Vol. 29, p. 179 (1900).

† Ugeton, *Proc. Roy. Soc. A*, Vol. 102, p. 400 (1923).

The mass of gas Q flowing through the tube per second is therefore

$$Q = \pi a^2 u_0 \rho = \frac{2\pi a^3}{lf} \frac{(p_1 - p_2)}{c} \\ = \frac{\pi a^3}{2l} \frac{(p_1 - p_2)}{f} \sqrt{\frac{2\pi M}{RT}} \quad \dots \quad (37)$$

The flow of gas through a tube at low pressures therefore differs considerably from that at high pressures, being dependent upon a^3 and the pressure difference $(p_1 - p_2)$ instead of a^4 and the difference in the squares of the pressures $(p_1^2 - p_2^2)$ (see Chapter XII, § 11, p. 282).

From more detailed considerations,* for a uniform tube of any circumference O and area of cross-section A , the mass of gas streaming through per second is given by

$$Q = \frac{(p_1 - p_2)}{8 \sqrt{\frac{\pi}{2} \frac{O}{A^3}}} \sqrt{\frac{M}{RT}} \quad \dots \quad (38)$$

which for a tube of circular cross-section differs from that in equation (37) only by a small numerical factor.

Equation (38) has been tested experimentally by Knudsen, using tubes ranging from 10^{-2} to 10^{-3} cm. in radius and from 2 to 12 cm. long. The results are in good agreement with the theory.

At intermediate pressures conditions are more complicated, the general relation for the mass of gas Q flowing through the tube per second being given by †

$$Q = \frac{\pi a^3}{8l\eta} (p_1 - p_2) \frac{M}{RT} p \left(1 + \frac{4\eta}{\xi a} \right), \quad \dots \quad (39)$$

where p is the mean pressure and ξ the coefficient of slip defined in equation (29), p. 203.

It can be shown that more accurate analysis gives equation (37) in the form

$$Q = - \frac{16}{3} \cdot \frac{a^3}{c} \cdot \frac{dp}{dx}$$

Putting $p = vkT = \pi v m \bar{c}^2 / 8$, we have

$$\frac{dp}{dx} = \frac{\pi m \bar{c}^2}{8} \cdot \frac{dv}{dx}$$

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 93.

† Loeb, *Kinetic Theory of Gases*, p. 253 (McGraw-Hill, 1927).

If q is the mass transferred per unit area of cross-section of the tube,

$$q = \frac{Q}{at} = -\frac{1}{2}an\bar{c} \frac{dv}{dx}.$$

Since the diffusion coefficient D is defined by

$$q = -Dn \frac{dv}{dx}$$

from the above equations we have

$$D = \frac{1}{2}a\bar{c}.$$

Individual steps in the total molecular path traversed are regarded as terminated either by collision with the tube wall or with other molecules. If l is the average step size, and the mean step sizes for wall and gas collisions are l_w and l_g respectively, regarding the total collision frequency as the sum of the individual collision frequencies we have

$$\frac{1}{l} = \frac{1}{l_w} + \frac{1}{l_g}.$$

Defining total and partial diffusion coefficients similarly by D , D_w and D_g , and taking each of these as proportional to the appropriate step sizes multiplied by \bar{c} , we have

$$\frac{1}{D} = \frac{1}{D_w} + \frac{1}{D_g}.$$

Since $D_w = 2a\bar{c}/3$ and $D_g \sim \lambda\bar{c}/3$, we obtain a general intermediate formula

$$D = \frac{2}{3} \frac{a\bar{c}}{1 + 2a/\lambda},$$

which reduces to the low-pressure or high-pressure formula according as $\lambda \gg a$ or $\lambda \ll a$. For a tube of finite length l , Pollard and Present have shown that at low pressures the diffusion coefficient is reduced by a factor $(1 - 3a/4L)$.

(v) Conduction of heat at low pressures.

It has been observed in § 2, p. 194, that the treatment of heat conduction on the simple kinetic theory is not so satisfactory as that of viscosity, partly because the quantity transported is a function of the gas-kinetic velocity and partly because Maxwell's distribution law is strictly true only for a gas in equilibrium. We consider the conduction of heat between two plates at temperatures T_1 and T_2 ; since $\lambda \gg d$, we note that the molecules which leave either plate arrive at the

opposite plate without disturbance by collision with other molecules. The net heat transferred per unit area per second is therefore

$$\begin{aligned}\Delta Q &= \frac{1}{2} \bar{v} \bar{c} n C_v (T_2 - T_1) f \\ &= \frac{1}{2} \rho \bar{c} C_v (T_2 - T_1) f. \quad \dots \quad (40)\end{aligned}$$

Equation (40) has been tested by Knudsen for a large number of gases, and the linear relation between conductivity and pressure extends up to 5×10^{-2} mm. for hydrogen. The quantity of heat transferred depends directly upon the pressure, in contrast to the conductivity at ordinary pressures, which is independent of the pressure. This property is made the basis of the Pirani pressure gauge described on p. 231.

It will be observed that the temperature gradient vanishes; Q is therefore no longer dependent on the temperature gradient but depends solely on the temperature difference between the two surfaces.

This may be demonstrated by stretching a tungsten wire down the centre of a tube in the middle of which a large bulb is blown. The wire is sealed in at the ends of the tube and heated electrically to yellow heat. A small side tube leads to a vacuum pump. At atmospheric pressure the quantity of heat lost by the wire in conduction across the gas to the glass container depends directly on the temperature gradient. The wire in the centre of the bulb therefore glows much more brightly than that in the narrow tubes. As the pressure is reduced, however, the conductivity depends progressively less on the temperature gradient, and at low pressures the wire glows practically uniformly along its entire length.

(vi) *Conduction of heat at intermediate pressures.*

Proceeding as on p. 202, we divide the gas into two regions, that up to a distance λ from the plates obeying the low pressure law and the main bulk of the gas obeying the ordinary pressure law. Evaluating the expressions for the heat conducted in the two regions and equating the expressions at the boundary at a distance λ from one of the plates, we find that the temperature gradient at intermediate pressures is

$$\frac{dT}{dx} = \frac{T_1 - T_2}{d + 2\lambda(2 - f)/f} \quad \dots \quad (41)$$

Substitution of this formula in equation (14), p. 198, gives, for unit area,

$$\Delta Q = \frac{1}{2} \rho \bar{c} \lambda C_v \frac{T_1 - T_2}{d + 2\lambda(2 - f)/f} \quad \dots \quad (42)$$

If $d \gg \lambda$, that is, at moderate pressures, equation (42) reduces to the formula for conduction at moderate pressures, as required, whereas at low pressures, where $d \ll \lambda$, equation (42) reduces to equation (40), except for a numerical factor and the way in which f is involved.

(vii) *Thermal effusion at low pressures.*

If a vessel containing a gas at low pressure is separated into two regions by a partition containing a small hole and the two regions are maintained at different temperatures T_1 and T_2 , the condition for equilibrium is no longer that the pressure shall be the same on both sides of the partition. Equilibrium is established when the number of molecules passing in either direction across unit area per second is the same, that is, when

$$\frac{1}{2}v_1\bar{c}_1 = \frac{1}{2}v_2\bar{c}_2,$$

by equation (20). Hence the ratio of the pressures is given by

$$\frac{p_1}{p_2} = \frac{v_1\bar{c}_1^2}{v_2\bar{c}_2^2} = \frac{\bar{c}_1^2}{\bar{c}_2^2} = \sqrt{\frac{T_1}{T_2}}. \quad \dots \quad (43)$$

The extra speed of the molecules on the high-temperature side therefore balances their lower number, so that as many arrive at the aperture per second as from the cooler side. The same relation holds if the aperture is replaced by a tube, because in the steady state $v\bar{c}$ is constant for all sections of the tube.

(viii) *Thermal transpiration at intermediate and higher pressures.*

At higher pressures equilibrium at an aperture in a plate occurs only when the pressure on the two sides is the same. Hence

$$\frac{1}{2}v_1\bar{c}_1^2 = \frac{1}{2}v_2\bar{c}_2^2,$$

which simply shows that the densities are inversely proportional to the absolute temperatures. If, however, a tube separates the two regions, conditions are more complicated. Consider any cross-section perpendicular to the axis of the tube, the latter being the x -axis, where the mean gas-kinetic velocity of the molecules is \bar{c} . On the average, the molecules crossing the layer per second will be those at a distance originally equal to the mean free path. The net number of molecules crossing unit area per second will, if we use Joule's classification, be

$$\begin{aligned} n &= \left[\frac{v\bar{c}}{6} + \frac{\partial}{\partial x} \left(\frac{v\bar{c}}{6} \right) \lambda \right] - \left[\frac{v\bar{c}}{6} - \frac{\partial}{\partial x} \left(\frac{v\bar{c}}{6} \right) \lambda \right] \\ &= \frac{v\lambda\bar{c}}{3} \left(\frac{1}{v} \frac{\partial v}{\partial x} + \frac{1}{\bar{c}} \frac{\partial \bar{c}}{\partial x} \right). \quad \dots \quad (44) \end{aligned}$$

Now

$$p = \frac{\pi}{8} m v \bar{c}^2. \quad \dots \quad (45)$$

Therefore

$$\begin{aligned}\frac{\partial p}{\partial x} &= \frac{\pi}{8} m \bar{c}^3 \frac{\partial v}{\partial x} + \frac{\pi}{4} v m \bar{c} \frac{\partial \bar{c}}{\partial x} \\ &= p \left(\frac{1}{v} \frac{\partial v}{\partial x} + \frac{2}{\bar{c}} \frac{\partial \bar{c}}{\partial x} \right). \quad (46)\end{aligned}$$

Since $\eta = \frac{1}{3} v m \lambda \bar{c}$ approximately, if we substitute for $\frac{1}{v} \frac{\partial v}{\partial x}$ from equation (46) in equation (44), we find that the mass of gas Q flowing per second through the tube is

$$Q = \pi a^2 \eta m = \pi a^2 \eta \left(\frac{1}{p} \frac{\partial p}{\partial x} - \frac{1}{\bar{c}} \frac{\partial \bar{c}}{\partial x} \right).$$

Further, since $\bar{c} \propto T^{\frac{1}{2}}$,

$$Q = \pi a^2 \eta \left(\frac{1}{p} \frac{\partial p}{\partial x} - \frac{1}{2T} \frac{\partial T}{\partial x} \right). \quad (47)$$

Now if the pressure difference between the ends of the tube is small, the application of Poiseuille's equation for the flow of gas through a tube (p. 282) gives

$$Q = - \frac{\pi a^4}{8\eta} \frac{\partial p}{\partial x} \frac{Mp}{RT}, \quad (48)$$

where M is the molecular weight of the gas. Hence, for the steady state, by equating (47) and (48), we have

$$\pi a^2 \eta \left(\frac{1}{p} \frac{\partial p}{\partial x} - \frac{1}{2T} \frac{\partial T}{\partial x} \right) = - \frac{\pi a^4}{8\eta} \frac{\partial p}{\partial x} \frac{Mp}{RT}$$

that is

$$\frac{\partial p}{\partial T} \left(\frac{2\eta^2 T}{p} + \frac{Mp a^2}{4R} \right) = \eta^2,$$

or

$$\frac{\partial p}{\partial T} = \frac{\eta^2}{2\eta^2 T/p + Mpa^2/4R}. \quad (49)$$

At low pressures equation (49) reduces to

$$\frac{\partial p}{\partial T} = \frac{p}{2T}$$

Hence p is independent of the nature of the gas and varies as $T^{\frac{1}{2}}$, as has already been shown by equation (43), p. 208. At higher pressures $p/\partial T$ is observed to be inversely proportional to the pressure and the molecular weight of the gas.

4. Properties of Gases at High Pressures; the Size of the Molecules.

The failure of the gas laws deduced for ordinary pressures when applied to gases at low pressures is due to the mean free path becoming comparable with or greater than the size of the container. At high pressures, the disagreement between simple theory and experiment is due to the failure of the second, third and fourth basic assumptions of Clausius, enumerated in § 1, p. 194. As the density of the gas increases, it is no longer possible to ignore the volume occupied by the molecules themselves or the mutual forces of attraction or repulsion that exist between them. The simple equation $pV = RT$ for a perfect gas has to be replaced at higher pressures by a more general equation of state; one such equation is that given by Van der Waals:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (50)$$

This equation will now be deduced from the kinetic theory and the significance of the constants a and b will be determined.

(i) *Finite size of the molecules and the significance of b .*

If we represent the molecular diameter and radius by σ and r , it is shown in the solution of Ex. 9, p. 323, that the mean free path is reduced in the ratio

$$\frac{\lambda_r}{\lambda} = \frac{V - 4(4\pi r^2 n/3)}{V} = \frac{V - b}{V} \quad . . (51)$$

Since the volume of the n molecules themselves is $c = 4\pi r^2 n/3$, we have $b = 4c$.

(ii) *Forces of attraction and repulsion between the molecules and finite time of collision.*

If the forces of attraction and repulsion between the molecules extend over a finite distance from each molecule, the collision will occupy a finite interval of time. Hence the number of collisions against the wall of the containing vessel in unit time will be reduced according to the equation

$$P = \frac{1}{3} \frac{C^2}{(V - b)} \frac{1}{(1 + \pi\tau)} \quad (52)$$

where τ is the time occupied in one collision and n is the number of collisions per second. Equation (52) may be written in the form

$$p(1 + \pi\tau) = \frac{1}{3} \frac{C^2}{(V - b)}$$

Now n is approximately equal to $\pi\sigma^2\bar{c}\tau$, since this represents the number of encounters made by a molecule of effective diameter σ in one second if the other molecules are treated as points. Hence, since $p = \frac{1}{3}\rho\bar{c}^2$ approximately, we have

$$p + \frac{1}{3}\rho\bar{c}^2\pi\sigma^2\bar{c}\tau = \frac{1}{3}\frac{\rho\bar{c}^2}{(\bar{V}-b)},$$

or

$$p + \frac{\pi^2}{8}\rho^2\frac{\sigma^2\bar{c}^2\tau}{n} = \frac{1}{3}\frac{\rho\bar{c}^2}{(\bar{V}-b)}, \quad \dots (52a)$$

and since $\rho \propto 1/\bar{V}$,

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V}-b) = \frac{1}{3}\bar{c}^2, \quad \dots (53)$$

where a is proportional to the coefficient of ρ^2 in the second term on the left-hand side of equation (52a).

A more powerful method of attack for such problems was developed by Clausius and is known as the *Virial Theorem*. (See Roberts, *Heat and Thermodynamics*, fourth edition, Chapter XXIII.)

(iii) Dependence of η on the size of the molecules.

By the method of dimensions it is possible to deduce the law of force between the molecules if the variation of the coefficient of viscosity with temperature is determined experimentally. Let the molecules repel one another at small distances apart with a force F given by

$$F = \mu r^{-s}, \quad \dots (54)$$

where r is the distance between the molecules, s is the required power, and μ is defined by equation (54). The coefficient of viscosity may be assumed to depend upon m , \bar{c} , μ and s , hence

$$\eta = f(m, \bar{c}, \mu, s) = \text{const. } m^\alpha \bar{c}^\beta \mu^\gamma, \quad \dots (55)$$

Since s is dimensionless, if we write equation (55) in dimensional form we have

$$ML^{-1}T^{-1} = M^\alpha L^\beta T^{-\beta} M^\gamma L^{(s+1)\gamma} T^{-2\gamma}.$$

Equating indices and solving in terms of s , we have $\alpha = (s+1)/(s-1)$, $\beta = (s+3)/(s-1)$ and $\gamma = -2/(s-1)$. Hence

$$\eta \propto (m^{(s+1)} \bar{c}^{(s+3)} \mu^{-2})^{1/(s-1)}. \quad \dots (56)$$

If it is observed experimentally that $\eta \propto T^n$, since $T \propto \bar{c}^2$ we have

$$2n = (s+3)/(s-1). \quad \dots (57)$$

Now for helium $n = 0.68$, hence $s \sim 12$, which indicates an extremely rapid rate of fall in the force as the distance from the molecule is increased, such as we might expect for a small, compact unit like the helium molecule. For carbon dioxide, however, which has a comparatively loose and open structure, $n = 0.98$ and hence $s \sim 5.2$, showing that the force extends over a comparatively large region.

From some aspects the behaviour of the molecules indicates that they may be regarded as having a hard core of radius proportional to a quantity denoted by σ_∞ , since at T_∞ the molecules will interpenetrate at each collision until the cores come into contact. Sutherland suggests that the value of σ at any other temperature T will be given by

$$\sigma^2 = \sigma_\infty^2 (1 + A/T), \quad \dots \dots (58)$$

where A is a constant. By equation (2), p. 191, therefore, the mean free path changes in the ratio

$$\frac{\lambda_T}{\lambda_0} = \frac{\sigma_\infty^2}{\sigma_T^2} = \frac{(1 + A/273)}{(1 + A/T)}, \quad \dots \dots (59)$$

where λ_0 is the mean free path at 0°C . Hence the ratio of the viscosity at any temperature T and the viscosity at 0°C will be

$$\frac{\eta}{\eta_0} = \frac{(\delta\lambda)_T}{(\delta\lambda)_0} = \left(\frac{T}{273}\right)^{3/2} \frac{A + 273}{A + T}. \quad \dots (60)$$

Formula (60) has been tested for nitrogen by Bestelmeyer and is in satisfactory agreement with experiment for temperatures between 90°C . and 300°C . It is, however, by no means rigorously obeyed by all gases, and fails completely at low temperatures.

5. Determination of Loschmidt's Number and the Molecular Diameter.

(i) *Loschmidt's deduction*

Since the mean free path is known from Maxwell's work on the viscosity of the gas, a determination of either v or σ and the use of equation (2), p. 194, enables us to evaluate both quantities. The value of v was first deduced in 1865 by Loschmidt by considering that in the liquid state all the molecules are as tightly packed as hard spheres can possibly be. The volume occupied by v such molecules is $v\sigma^3/\sqrt{2}$, for the packing will be tetrahedral. Hence if the densities of gas and liquefied gas are δ and Δ respectively, we have

$$\frac{\delta}{\Delta} = \frac{v\sigma^3}{\sqrt{2}} \quad \dots \dots (61)$$

From equations (2) and (61), therefore,

$$v = \frac{1}{2\pi^2\lambda^3} \left(\frac{\Delta}{\delta}\right)^2 \quad \dots \dots (62)$$

The value obtained was $\nu = 10^{18}$ mols./c.c., a result which is now known to be about twenty times too low. The value of α deduced, about 10^{-7} cm., was therefore about 5 times too great, but the deductions were of great value in fixing the order of the quantities involved.

(ii) *The Brownian movement and the kinetic theory of liquids.*

The kinetic theory of matter receives quite independent and most spectacular support from the discovery made by Brown in 1827. Using the then new achromatic objective, Brown observed that small particles about 10^{-3} mm. in diameter, such as pollen grains, when held in sus-

pension in a liquid, exhibit unceasing irregular motion in all directions. Initially the phenomenon was ascribed to vital forces, but subsequent work showed that it was also exhibited by small particles held in suspension in the liquid inclusions in granite and other rocks of great age. Not until nearly fifty years after its discovery was it suggested by Wiener and later more convincingly by Delsaulx that the Brownian movement is a visible demonstration of the validity of the kinetic theory of liquids. In any small interval of time a particle will receive more impacts from molecular bombardment on one side than another. If the particle is sufficiently small, it will therefore execute a small motion under the resultant force until its path is altered by further impacts. The observed motion under the microscope is merely the resultant path of a large number of zigzag paths which are each too small to be resolved by the microscope and the eye. The experiments on the Brownian movement are of several types; of those described below, the first has been applied to liquids and the second to liquids and gases.

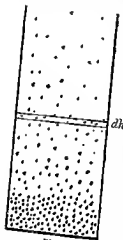


Fig. 4

(a) *Sedimentation equilibrium.*

Sedimentation equilibrium is established when a suspension, emulsion, or colloidal solution is contained in a vertical vessel. Under the opposing influences of osmotic pressure, which on the kinetic theory arises from the bombardment of the molecules, and gravity, a definite vertical concentration gradient is established in the steady state. Referring to fig. 4, we see that if ν represents the number of suspended particles per unit volume at a height h above the bottom of the container, the increase in osmotic pressure dp due to the increase

in the number of particles at a height ($h - dh$) must be sufficient to balance the weight of the particles. Hence

$$dp = vmg dh, \quad \dots \dots \dots (63)$$

where m is the mass of each particle* (all the particles being assumed identical) and g is the acceleration due to gravity. Further,

$$p = \nu kT, \quad \dots \dots \dots (64)$$

where k is Boltzmann's constant (p. 182) and T is the absolute temperature. Hence

$$dp = kT d\nu, \quad \dots \dots \dots (65)$$

and from equations (63) and (65) we have

$$\frac{d\nu}{\nu} = \frac{mg}{kT} dh \quad \dots \dots \dots (66)$$

Integrating between heights h_2 and h_1 , where the numbers of particles per unit volume are ν_2 and ν_1 respectively, we obtain

$$\log_e \frac{\nu_2}{\nu_1} = \frac{mgN}{RT} (h_2 - h_1), \quad \dots \dots \dots (67)$$

where N is Avogadro's number, 6.06×10^{23} molecules per gramme-molecule, and R is the gas constant referred to one gramme-molecule.

The classical series of experiments on equation (67) was carried out by Perrin between 1909 and 1912. Emulsions of gamboge or mastic were subjected to continuous centrifuging for a month at the rate of 3000 revs./min., the spherical particles being in this way separated into layers containing particles of the same size. A drop of the emulsion was then placed on a microscope slide so as to form a column about 1/10 mm. high, which was then observed with a powerful objective from above. With visual observations it was necessary to hunt the field by the use of a plate with a fine hole, otherwise at any instant more particles filled the field than could be counted at a single glance. Great care had to be taken to filter out the heat rays (by using water cells) from the beam of light, which was incident in a horizontal direction. Any inequality of temperature in different parts of the emulsion produced convection currents in the liquid, which were much greater than the Brownian movement. These precautions are even more necessary in the determination of N by the dynamical method discussed later.

On the average about five particles were visible at any instant and a large number of readings were required to eliminate statistical errors. It was found possible, however, to reduce the labour by a factor of 200 by using a powerful

very thin layer was observed for one position of the microscope. After sufficient readings had been taken the microscope was racked up a distance d measured

* m is, of course, the reduced mass where allowance has been made for the buoyancy.

on an accurately graduated vernier and another set of readings was taken, the distance ($h_2 - h_1$) being determined from the expression μd , where μ was the refractive index of the emulsion.

To determine the remaining quantity m of equation (67), the volume and density of the grains were obtained by the following methods.

(1) *Density of the grains.*

- (a) Specific gravity bottle.
- (b) Surrounding the grains by potassium bromide of increasing concentration until the grains neither floated nor sank, when the density of grains and solution was the same.
- (c) Adding potassium bromide solution until the grains did not separate on centrifuging.

(2) *Volume of the grains.*

- (a) Direct determination of the radius by allowing the emulsion almost to dry on a glass plate. The grains were then pulled into rows by surface tension and the length of a row and the number of grains contained in it were determined with a travelling microscope.
- (b) Application of Stokes's law (see Chap. XII, § 10, p. 280),

$$0.077v = \frac{2}{3}\pi r^2(D - d)g,$$

where r is the radius of the grains, D and d the density of the grains and liquid respectively, η the coefficient of viscosity of the emulsion, and v the terminal velocity, that is, the velocity with which the "edge" of the cloud of grains formed by stirring the emulsion descends under the influence of gravity. The terminal velocity was a few mm. per day, and the application of the uncorrected form of Stokes's law was considered valid, since the radius of the particles was much greater than the mean free path of the molecules in the liquid.

As a check on the results, the weight of the grains was determined in a number of cases by directly weighing a known number of grains which had been made to adhere to a glass plate immersed in the solution when the latter was made slightly acid.

From observations on many thousands of grains the final value $N = 6.8 \times 10^{22}$ mols./gram. mol. was obtained, a value some ten per cent greater than that accepted at present. Using the same method, but with colloidal particles of gold and silver, Westgren in 1915 obtained the value $N = 6.04 \times 10^{22}$, which is within one-half per cent of the accepted value.

(b) *Einstein and Smoluchowski's equation.*

In 1905, Einstein and Smoluchowski succeeded in deducing a relation between the mean square displacement of a particle undergoing Brownian movement and the time interval between two successive observations. Referring to fig. 5, let a uniform density gradient, increasing in the direction of the negative x -axis, be set up as a result of the fortuitous accumulation of a large number of particles in that region owing to the Brownian movement. We consider only motion parallel to the x -axis and divide the fluid into three shallow layers B , A , C at distances $-x$, 0 , and $+x$ from the origin. The number of particles present per unit volume at C is $\nu = \nu_0 - x(\partial\nu/\partial x)$ if the number present

in unit volume at A is v_0 . In a given time t a number of particles dv will experience a fortuitous variation of their co-ordinates by an amount lying between α and $\alpha + d\alpha$. Then

$$dv = f(\alpha) d\alpha, \quad \dots \dots \dots (68)$$

where it is required to find the nature of the function $f(\alpha)$. Quite generally $f(\alpha)$ must satisfy the two relations

$$f(-\alpha) = f(\alpha) \quad \dots \dots \dots (69)$$

and

$$\int_{-\infty}^{+\infty} f(\alpha) d\alpha = 1, \quad \dots \dots \dots (70)$$

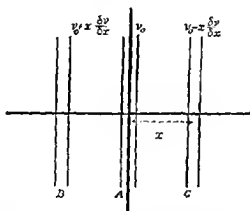


Fig. 2

since there are no preferred directions and the particle must be present somewhere

Applying equation (68) to the slices B and C , subtracting, and integrating, we obtain the number of particles crossing unit area of the plane at A if the integration is carried out (i) over all values of α from 0 to ∞ , since only particles passing towards A can be considered, (ii) over values of x less than α , since for a greater value of x the particle will not reach the plane at A on displacement. Hence, if the number of particles crossing unit area of A in time t is represented by nt , we have

$$nt = 2 \frac{\partial v}{\partial x} \int_0^{\infty} f(\alpha) d\alpha \int_0^{\alpha} x dx \quad \dots \dots \dots (71)$$

or, changing the limits,

$$nt = \frac{1}{2} \frac{\partial v}{\partial x} \int_{-\infty}^{+\infty} \alpha^2 f(\alpha) d\alpha. \quad \dots \dots \dots (72)$$

If $\bar{\alpha}^2$ represents the mean square displacement of the particles, since $\int_{-\infty}^{+\infty} f(a) da = 1$, we have

$$nt = \frac{1}{2} \bar{\alpha}^2 \frac{\partial v}{\partial x} \quad . \quad . \quad . \quad . \quad (73)$$

Equation (73) may be put into a more convenient form. Since

$$p = \nu kT$$

and the force on unit volume is equal to the gradient of the pressure, the force on each particle in unit volume is

$$F = \frac{1}{\nu} \frac{\partial p}{\partial x} = \frac{kT}{\nu} \frac{\partial v}{\partial x} \quad . \quad . \quad . \quad . \quad (74)$$

Now by Stokes's law

$$F = 6\pi\eta r v, \quad . \quad . \quad . \quad . \quad (75)$$

and the number of particles crossing unit area in unit time is

$$n = \nu v, \quad . \quad . \quad . \quad . \quad (76)$$

Hence from equations (73), (74), (75), and (76) we have

$$\bar{\alpha}^2 = \frac{RT}{3\pi\eta r N} t, \quad . \quad . \quad . \quad . \quad (77)$$

According to equation (77), which is Einstein's equation, therefore, the mean square displacement increases in proportion to the time which has elapsed since the last observation. By a similar analysis, the *mean square angular displacement* which the particles suffer as a result of rotational motions arising from the Brownian movement may be shown to be

$$\bar{A}^2 = \frac{RT}{4\pi r^3 \eta N} t, \quad . \quad . \quad . \quad . \quad (78)$$

Equations (77) and (78) have been tested by Perrin by observing the motion of particles with a microscope fitted with a transparent squared grating in the eyepiece. The rotational motion is followed by means of observations on an air inclusion in a particle: urea is a particularly useful substance for this experiment. Besides showing that $\bar{\alpha}^2$ is proportional to t , Perrin observed that the lengths of the paths are distributed according to a Maxwellian distribution law. Later experiments by Seddig confirmed those of Perrin and extended the range over a mass variation of 1 : 15,000.

The validity of Einstein's equation for particles suspended in gases was first investigated by Ehrenhaft and later by de Broglie. The most celebrated experiments are those of Millikan, in which an oil-drop is allowed to fall through a gas between the plates of a parallel plate condenser. With no electric field present, if the drop is small enough, it may readily be shown by observation with a microscope that $\bar{\alpha}^2 \propto t$. To avoid determining r , the drop is allowed to fall under gravity whence, applying Stokes's law, we have

$$6\pi\eta r v = \frac{4}{3}\pi r^3 (\rho - \sigma)g, \quad . \quad . \quad . \quad . \quad (79)$$

where ρ and σ are the densities of the oil and air respectively. The coefficient of viscosity of air has to be determined by a separate experiment (see Chapter XII, § 11, p. 281). If the drop reaches its position and the same drop.

The method has the following advantages over that with liquid emulsions:

- (i) a single particle may be observed for hours;
- (ii)
- (iii)
- (iv)

by lowering the pressure it may be made 100 times as great.

It may also be observed, as is shown by Ising,* that the sensitiveness of galvanometers reaches its limit when the suspension is so fine that the suspended system has no definite zero, owing to the Brownian movement imparted by the surrounding gas molecules. With a sufficiently thin fibre Gerlach obtained a Brownian movement of over 5 metre for the spot from a suspended mirror illuminated with a lamp at a distance of a metre from the scale. Continuing Gerlach's work, Kappler has deduced the value of Avogadro's number from a photographic record of the Brownian movement of the spot of light. Since the system has one degree of freedom, by the theorem of the equipartition of energy we have

$$\frac{1}{2}c\bar{\theta}^2 = \frac{1}{2}kT, \quad \dots \dots (80)$$

where $\bar{\theta}^2$ is the mean square deflection and c the restoring couple in the fibre for unit angle of twist. The value obtained for N is 6.06×10^{23} and is correct to within 1 per cent. Care had to be taken to reduce the effect of mechanical vibrations and convection currents; the reality of the effect was strikingly shown by the

only 10^{-4} gm

(c) Brillouin's diffusion experiments

If v_1 and v_2 represent the numbers of particles per unit volume in an emulsion, situated a distance apart equal to the root mean square displacement \bar{a} , in time t the net interchange of particles between the two regions is approximately

$$n = \frac{1}{2}\bar{a}(v_1 - v_2) \quad \dots \dots (81)$$

By the definition of the coefficient of diffusion D

$$n = D \frac{(v_1 - v_2)}{\bar{a}} t \quad \dots \dots (82)$$

Hence

$$\bar{a}^2 = 2Dt, \quad \dots \dots (83)$$

* Ann. d. Physik, Vol. 14 (7), p. 755 (1932).

or, from equations (77) and (83),

$$N = \frac{RT}{D} \frac{1}{6\pi\eta r}, \quad \dots \dots \dots (84)$$

To test these relations, Brillouin used a suspension of gamboge in glycerine, in which was immersed a glass plate which acted as a perfect absorber for all grains coming into contact with it. If ν represents the average number of grains per unit volume of the emulsion, the number of particles absorbed per unit area of the plate in time t will be

$$n = \frac{1}{2}\nu\bar{x}, \quad \dots \dots \dots (85)$$

since the probability that the particles will be displaced towards the plate is equal to $\frac{1}{2}$. From equations (83) and (85), therefore, we have

$$n^2 = \frac{1}{2}D\nu^2t, \quad \dots \dots \dots (86)$$

i.e. the square of the number of grains collected should be proportional to the time. Examination of photographs of the glass plate, taken at regular intervals of time, showed agreement with (86) and gave the value 6.9×10^{13} for N .

The breadth of the tracks of ionizing particles in a cloud chamber apparatus illustrates the general validity of equation (83), as applied to the diffusion of ions in a gas, recombination being neglected. Using a counter-controlled cloud chamber, Blackett has shown that the breadth of the tracks is proportional to the square root of the time which elapses between the liberation of the ions and their fixation by water drops. Similarly, since the diffusion coefficient is inversely proportional to the pressure at the usual pressures used in cloud chambers, according to equation (83) the track breadth is inversely proportional to the square root of the pressure.

The separation of isotopes of the elements affords another practical application of diffusion theory. For a gas composed of two groups of molecules of masses M_1 and M_2 , but at the same uniform temperature and pressure throughout, the average kinetic energy of the two groups is the same. Hence if C_1^2 and C_2^2 are the corresponding mean square velocities, then $\frac{1}{2}M_1C_1^2 = \frac{1}{2}M_2C_2^2$. The mean velocities are therefore proportional to the reciprocal of the square root of the corresponding masses and, since the mean free paths are approximately the same if we neglect the small difference in molecular diameter, the diffusion coefficient is by equation (19) proportional to C and hence to $M^{-1/2}$. Consequently, if gas is passed along a porous tube, the lighter constituent will diffuse more rapidly than the heavier and the immediate separation factor is given by $(M_2/M_1)^{1/2}$. Effective separation in lighter elements like hydrogen and deuterium, and of the two neon isotopes 20 and 22, has been carried out in this way. With neon Hertz used 48 porous tubes in series and 24 pumps, and the diffusate was repeatedly re-cycled. In a few hours a 99 per cent separation of over 50 a.e. of the lighter isotope was obtained. With the two isotopes of uranium 235 and 238 the separation factor is very nearly unity, but separation has been effected using the gas uranium hexafluoride, acres of diffusion wall and thousands of pumps.

Thermal diffusion processes may be used both in gases and liquids but, because of the high temperature required, corrosion is often a great practical difficulty. Originally introduced by Clausius and Dickel, the apparatus consisted of a tube some 35 m. long with a central wire maintained at 600° C. The two chlorine isotopes 35 and 37 gave a 99 per cent separation for 8 a.e. in 24 hours. The separation is not governed by simple diffusion theory but depends to such an extent on intermolecular forces that variations in temperature or concentration may decide whether the lighter or heavier isotope will eventually collect near the cooler surface.

Concentration of solution 1870 shows that $\epsilon = 0.001$.

centrifuge is given by equation (67) as $\exp[(M_2 - M_1)v^2/2RT]$, where $r = (b_2 - b_1)$, and g has been replaced by $v^2/2r$, the average acceleration between the centre and the periphery. The separation factor depends therefore on the differ-

chlorine 37 isotope was enriched by 5 per cent. Likewise Humphreys, using the Beams type vacuum air-driven ultra-centrifuge, obtained an increase of 11 per cent in bromine 79 compared with bromine 81, using bromine vapour.

(d) *Fluctuations in fluids.*

If the actual number of particles present in a given volume is n and the average number taken over a long time is \bar{n} , the average relative fluctuation is defined by

$$\epsilon = \frac{n - \bar{n}}{\bar{n}}. \quad (87)$$

From the probability calculus, Smoluchowski * showed that

$$\epsilon = \sqrt{\frac{2}{\pi \bar{n}}} \quad (88)$$

and hence, since the fluctuation in a volume containing 10,000 particles is about 1 per cent, the effect should be observable in fluids near the critical point. The effect manifests itself experimentally as *critical opalescence*.

The opalescence, which, as we see, is constant with time, is explained on the molecular view by the fortuitous gathering of a large number of molecules in various places in the fluid, as a result of thermal agitation. The groups of molecules are large enough to scatter light appreciably, and since they are continually breaking up and forming fresh groups, a shimmering opalescence is produced.

Combining Rayleigh's formula for the scattering of light by small obstacles with Smoluchowski's investigations on critical opalescence, Keenan † has derived the equation

$$\epsilon = \frac{\pi^2}{18} \frac{1}{\lambda^4} \frac{RT}{N} (\mu_0^2 - 1)^2 (\mu_0^2 + 2)^2 \left(-\frac{1}{v_0} \frac{\partial v_0}{\partial p} \right), \quad (89)$$

* See Firth, *Schwingungserrechnungen in der Physik* (Sammlung Vieweg, Part 48, Brunswick, 1920)

† J. Keenan, *Atoms* (Constable & Co. Ltd., 1923)

where i is the fraction of the intensity of the light scattered per c.c. in a direction perpendicular to the incident beam, μ_0 is the refractive index of the fluid for light of wave-length λ in free space, v_0 is the specific volume of the liquid, and $\partial p/\partial v_0$ its isothermal compressibility. Experiments by Keesom and Kamerlingh Onnes on ethylene at 11-18° abs. gave a value for N equal to 7.5×10^{22} mols./gramme-molecule.

(c) *Size of molecules from Van der Waals' equation.*

The size of the molecules of a gas may be determined directly in two ways from Van der Waals' equation, provided the value of N is known. Thus, if the critical volume V_c is measured directly, since $V_c = 3b$, by Van der Waals' equation,* and $b = \frac{2}{3}\pi\sigma^3n$, σ is obtained. The method is not accurate, for V_c is difficult to measure experimentally; further, the relation $V_c = 4b$ is shown to be in better agreement with the experimental results.

According to Van der Waals, however,

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (90)$$

under any conditions. Hence, if $\frac{1}{p_0} \left(\frac{\partial p}{\partial T}\right)_v$ represents the coefficient of pressure increase of the gas at constant volume,

$$\frac{1}{p_0} \left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{T_0} \left(1 + \frac{a}{p_0 V^2}\right), \quad (91)$$

from which the value of a is obtained. Further, if $\frac{1}{V_0} \left(\frac{\partial V}{\partial T}\right)_p$ represents the coefficient of volume increase at constant pressure, from equation (90) we have approximately

$$\frac{1}{V_0} \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T_0} \left[1 + \frac{a}{pV_0} \left(\frac{1}{V_0} + \frac{1}{V}\right) - \frac{b}{V_0}\right]. \quad . (92)$$

The value of a having been obtained from equation (91), the value of b is finally given by equation (92).

6. Production of High Vacua.

The maintenance of a high vacuum depends on the freedom of the system from leaks; the whole apparatus must therefore be free from joins and, in general, consist of glass throughout, or of metal and glass directly sealed together where necessary. The speed with which the vacuum is obtained, apart from the nature of the pump, also depends on the breadth and length of the connecting tubes. Examination of equation (37), p. 205, shows that at low pressures the rate of flow of gas is inversely proportional to the length and directly proportional to the

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 110.

cube of the radius of the tube. Finally, the degree of vacuum obtainable and its measured value will depend on the vapour pressures of the materials in the pump (e.g. oil) and pressure gauge (e.g. mercury) respectively.

The pumps used for the production of low pressures may be broadly divided into two groups, according as their action is purely mechanical or depends on the molecular and kinetic properties of the gas. It is now possible to obtain mechanical pumps, such as the Geryk "R.L." type, which by almost complete elimination of oil vapour will produce a vacuum of 10^{-3} mm. of mercury; * again, a mercury pump of the Sprengel or Töpler type, although tedious to use, will produce a vacuum of the same order if a liquid-air trap is inserted between the mercury and the vessel which is being exhausted, to prevent access of mercury

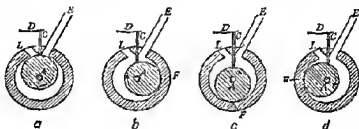


Fig. 6

vapour to the evacuated system. In general, however, mechanical pumps produce vacua only of the order of 5×10^{-3} mm., but their use is essential to provide a fore-vacuum or "backing" for the molecular pumps.

(a) Cenco-Hyvac pump.

As an example of a convenient mechanical pump, the Cenco-Hyvac pump (figs. 6(a) to (d)) will now be described. The rotor *G* is mounted eccentrically in the cylinder, and four successive positions are shown. In the side of the outer cylinder

arm *D*,
the valve
the pump
fig. 6(a),

second position, the gas is in process of being compressed as the eccentric rotor

rotates, and the gas is being admitted behind the rotor. Further compression

17
g
n
s

* In future, mm. will refer to mm. of mercury

(b) *Gaede molecular pump.*

It has been shown in § 3, p. 200, that when the mean free path λ of the molecules is greater than the linear dimensions of the apparatus, the molecules acquire the properties of the walls of the apparatus and do not dissipate those properties rapidly by subsequent intramolecular collisions. If, therefore, the gas molecules in a fore-vacuum are allowed to come into contact with a rapidly moving surface, they will to some extent acquire the drift velocity of that surface. If the distance between two parallel boundary planes is d , one of the planes being fixed and the other moving, it may be shown that at low pressures the ratio of the gas pressures at two points a distance l apart measured in the direction of motion is

$$\frac{p_2}{p_1} = \frac{d}{d'} \dots \dots \dots (93)$$

where c is a constant. For a given velocity it is the ratio of the initial and final pressures which is constant; the fore-vacuum should therefore be as high as possible.

The principle of the apparatus is shown in fig. 7, where the evacuated system and the exhaust are connected to V and Z respectively. The cylinder A rotates in the outer cylinder T , evacuation resulting from molecules being projected along the groove VZ after impact with the revolving cylinder A . At a speed of 12,000 revs./min. the vacuum attainable is less than 10^{-6} mm. with a fore-vacuum of 1.2 mm.

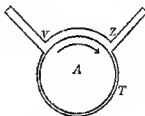


FIG. 7

(c) *Mercury vapour pumps.*

As is well known, the passage of a steam or mercury vapour jet up the tube AB (fig. 8) gives rise to a vacuum in the system on the right. The pumping process depends on the relative rates of diffusion of the vapour of the jet and the gas through the porous plug. A large increase in efficiency is obtained by the introduction of the vapour trap cooled by water or liquid air. The principle was first applied by Gaede, who called the apparatus a *diffusion pump*. The porous plug was replaced by an adjustable slit, since it was found that the apparatus has maximum efficiency when the width of the slit is approximately equal to λ , the mean free path of the gas molecules. Further, the maximum effect is obtained when the pressure of the mercury vapour is just greater than that of the fore-vacuum. Vacua of less than 10^{-6} mm. may be obtained, but while theoretically there is no limit to the vacuum attainable, in practice two disadvantages arise: (a) the exhaust speed is slow, (b) careful regulation of the temperature of the mercury vapour is required.

By a modification of the Gaede diffusion pump, by which it became a *condensation pump*, Langmuir eliminated both these disadvantages. The main advance consists in cooling the mercury vapour thoroughly at the jet, so that condensation occurs, back diffusion of the mercury vapour thereby being completely eliminated. The apparatus has the advantage of requiring no critical conditions and the size of the orifice may vary over a wide range.

A convenient form is shown in fig. 3, mercury is heated in the Pyrex glass bulb *A*, the vapour rising in the curved tube *B*. Condensation of the vapour is prevented by the asbestos lagging *H* until the vapour issues from the orifice *F*. The tube *L* is enclosed in another tube *C*, which is surrounded by a water jacket *J* fed by the tubes *K*. The gas is discharged through *N*. The mercury vapour condenses almost instantaneously, very little rising above a point such as *E*.

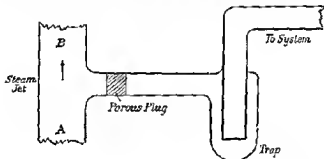


FIG. 3

The system to be evacuated is connected by the tube *K* to the liquid air trap *G* and thence by the cross-tube *F* to the tube *C*. The mercury collects in liquid form at *D* and is returned to the bulb *A* by the fine tube *M*. The pump is very efficient, reducing a pressure of 1 mm. to 10^{-4} mm. in 80 sec. with a speed of working of nearly 4 litres/sec.

Many varieties and sizes of commercial pump are now available which operate on the above principles, but in most cases the mercury has been replaced as the working substance by special oils such as those of the Apiezon group. Robust vessels of copper and brass contain the oil which is vaporized by electrical heating. High efficiency is ensured since the vapour pressure of these oils is extremely low at ordinary temperatures. The possibilities of metallic corrosion in various parts of the vacuum system are negligible compared with those when mercury is used. The high molecular weight of oil compared with that

expensive backing pumps to give a greater initial backing vacuum.

(d) *Other processes.*

To push the vacuum below 10^{-6} mm., methods other than pumping must be used. The commonest of these is a *sorption process*, in which the system is connected to a tube surrounded by liquid air and containing coconut charcoal which has been recently heated. The gas is absorbed by the charcoal and a pressure of 10^{-7} mm. may be obtained in this way. The rate of absorption is monomolecular. Gases such as nitrogen, carbon dioxide, ammonia and hydrogen may be readily removed. Hydrogen may also be eliminated by its affinity for palladium or platinum black.

Traces of oxygen and some other gases may be removed by the *chemical process* of "flashing", that is, vaporizing a metal such as magnesium or calcium in a vessel connected to the system; a compound of negligible vapour pressure is formed. Again, *thermal processes* may be employed; thus nitrogen is slowly removed in the presence of an incandescent tungsten filament. Finally, *electrical processes* are available either in the

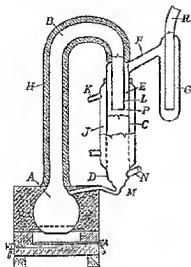


Fig. 9

form of the glow discharge or of impacts of electrons obtained thermionically. The action is generally considered to consist in ionization of the gas atoms or molecules, after which the ions adhere to the walls of the container, particularly if the latter is suitably cooled.

(e) *Pumping speeds.*

Since the number of gas molecules escaping through an aperture of unit area into a perfect vacuum in unit time is $\frac{1}{4}n\bar{c}$, substituting the appropriate quantities for air at 27°C . we obtain a figure of 11.7 litres per sec. The *speed factor* of an actual pump is defined as the ratio of the volume of gas passing through the throat of the pump per second to the above ideal figure. Mercury diffusion pumps such as those described in (c) have speed factors up to 0.3; for the more recent oil diffusion pumps it is nearer 0.5 or 0.6.

The effective pumping speed S at the end of the vacuum line will be less than S_0 because of the resistance W of the line, the relation between these quantities being $1/S = 1/S_0 + W$. From equation (37) W is proportional to l/a^3 ; the proportionality constant depends on the square root of the molecular weight, and it is approximately unity if the values are inserted for air, l and a are expressed in millimetres and W is then in seconds per litre.

The rate at which the pressure P is reduced in a given apparatus is, by application of Boyle's law, equal to $dP/dt = -S(P - P_0)/V$, where V is the volume of the apparatus and P_0 is the final limiting pressure attainable by the pump because of leaks and gas emission. The time taken for a vacuum system to recover its required pressure P_2 if a surge of gas has temporarily raised the pressure to P_1 , where both pressures are considerably greater than P_0 , is given by

$$t = \frac{V}{S} \log \frac{P_1}{P_2}$$

by integration of the preceding equation.

7. Measurement of Low Pressures.

Of the manometers described below, those under (a) and (b) are not directly dependent on molecular and kinetic properties of the gas, but are merely refined extensions of methods for measuring ordinary gas pressures. The remaining pressure gauges are all based on known theoretical laws connecting the measured property of the gas with its pressure.

(a) Mercury manometers.

A direct extension of the ordinary mercury manometer to the measurement of low pressures may be obtained by the use of the optical lever.

Fig. 10 shows an apparatus due to Carver; the mercury cut-off at A is initially open, and a tap (not shown) at the top of the gas tube cuts off the system whose

The standard instrument against which almost all manometers are

in practice calibrated is the *McLeod gauge*, which depends for its action on the validity of Boyle's law at low gas pressures.

Fig. 11 illustrates Gasde's modification of the McLeod gauge; gas from the system whose pressure is required enters the gauge through *B* and fills the gauge down to the level of the mercury reservoir. The reservoir *G* is then raised, cutting off the gas present in the bulb *H* and compressing it into the capillary extension, which lies along the scale *KK*. The mercury rises faster in the left-hand arm, and may be made to stand at any arbitrary height in the tube *A*, above that in the closed tube. Then if the gas pressure in the system is *p*, the volume of bulb and capillary *V*, the final pressure (*p* + *H*) and the final volume *V*₁, we have

$$pV = (p + H)V_1$$

or, since $p \ll H$,

$$p = \frac{HV_1}{V} \quad \dots \quad (94)$$

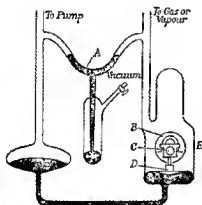


Fig. 10

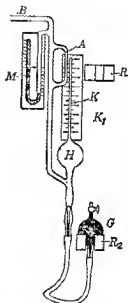


Fig. 11

An alternative method of using the gauge is to raise the reservoir between fixed positions (*R* and *R*₂ in the figure). When the reservoir is at *R*₂, the bulb and capillary are open to the system; when the reservoir is raised to *R*, the mercury always rises to the level in *A* corresponding to the top of the closed capillary and forming the zero of the scale *KK*. (The tube *A* and the closed capillary are of the same diameter, to avoid differences in pressure arising from the capillary depression of mercury in a narrow tube.) Then applying Boyle's law before and after compression, if *p* and *H* are measured in mm. and *V*₀ is the volume of 1 mm. length of the capillary tube, we have

$$pV = (p + H)HV_0$$

or, since $p \ll H$,

$$p = \frac{V_0 H^2}{V} \quad \dots \quad (95)$$

The scale *KK*, is graduated directly according to this parabolic law; a large range

of pressures is thus obtained on a relatively short scale. Pressures from 100 mm. to 1 mm. can be read directly on the manometer *M* and from 1 to 10^{-4} mm. on the scale *KK*₁.

The McLeod gauge measures pressures down to 10^{-5} mm., but of course the pressures include those of mercury vapour and other vapours, unless the latter are removed by suitable condensing traps.

(b) *Mechanical manometers.*

The common Bourdon brass spiral gauge has been applied to the measurement of low pressures by Ladenburg and others in the form of a spiral of thin glass tubing. The movement of the end of the spiral is registered by an attached mirror which allows the use of an optical lever. A null method is often used, external pressure being applied to bring the mirror back to its zero position; this external pressure is recorded by a McLeod gauge placed at a distance. The pressure of corrosive gases which attack mercury may be found in this way.

Alternatively, a type of aneroid barometer may be used in the form of a brass box containing a thin dividing membrane of copper. One side of the membrane is connected to a very high vacuum and the other side to the system whose pressure is required. The membrane presses against a glass plate, the system is illuminated, and the interference fringes are observed with a microscope. The apparatus is calibrated against the McLeod gauge.

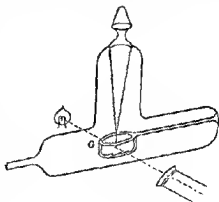


Fig. 12

(c) *Viscosity manometers.*

Reference to equation (23), p. 201, shows that at low pressures the viscous force existing between two surfaces in relative motion is directly proportional to the pressure of the gas and to the square root of its molecular weight. Manometers based on this relation are of two types, which depend on (a) the rate of damping of a vibrating system suspended in the gas, or (b) the steady torque communicated to a suspended surface placed opposite a surface in motion.

In Coshido's *quartz fibre manometer* (fig. 12) two fine quartz fibres are arranged in semi-lifilar suspension and end in a common tip, the vibratory motion of

which is observed by a microscope with a scale in the eyepiece. If we denote the logarithmic decrement, which is a measure of the total damping, by λ , the general relation will be

$$\lambda = a + bp\Delta T, \quad \dots \dots \dots (96)$$

where a represents the damping due to friction of the support and b is constant at constant temperature. The quantity a is determined from the residual damping when the system is completely exhausted. The apparatus is calibrated against the McLeod gauge; the linear relation is valid over the range 10^{-2} mm. to 10^{-3} mm.

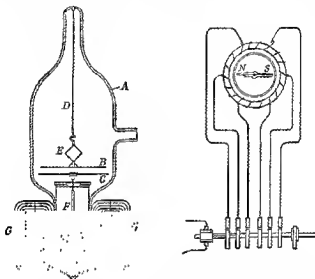


Fig. 12

In *Dushman's molecular gauge*, the viscous drag exerted when a disc O (fig. 13) is rotated rapidly at uniform speed close to a similar plate B suspended by a quartz fibre D is observed by means of a mirror E . The whole system is contained in the glass vessel A , and to ensure absence of leaks from the air the disc O is rotated by the effect of a rotating magnetic field in the Gramme ring GG on the magnet NS , fixed to the vertical axis F . If r_0 is the radius of the upper disc, and we consider a circular strip of radius r and $r + dr$, the total torque exerted by the lower disc, by equation 23, is

$$\begin{aligned} \tau\theta &= \int_0^{r_0} rK\omega r p \left(\frac{M}{RT}\right)^{\frac{1}{2}} 2\pi r dr \\ &= \frac{\pi K p \omega^2}{2} \left(\frac{M}{RT}\right)^{\frac{1}{2}}, \quad \dots \dots \dots (97) \end{aligned}$$

where K is a constant, θ the deflection produced, τ the restoring couple for unit angle of twist, and ω the angular velocity of rotation of the lower disc.

A more correct formula given by Dushman * is

$$\theta = \left(\frac{4\pi^2 D^2}{32\pi \delta} \right) p \omega \left(\frac{M}{RT} \right)^{1/2}, \quad \dots \dots (98)$$

where D is the diameter of the rotating disc C , δ and t are the moment of inertia and the period of natural oscillation of the disc B , and k is a constant involving the accommodation coefficient. Pressures down to 10^{-1} mm. may be measured with this apparatus, the usual range extending from 10^{-4} mm. By equation (98), the instrument may be used to measure pressure absolutely, but k is not usually known accurately, so the McLeod gauge is generally used for calibration.

(d) *Radiometer gauges.*

The common *Crookes radiometer* may be used to measure low gas pressures, but its operation is complicated and still doubtfully under-

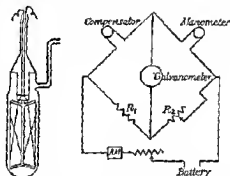


FIG. 14

stood. The explanation that the radiometric forces arise simply from the greater velocity of rebound of molecules from the surface at higher temperature is untenable, as this process would lead to a decrease in the density of the gas close to the surface, and a consequent reduction in the number of molecular impacts per second. It would appear that fresh gas is continually supplied to the centre of the hot surface by *thermal creep* in which, as Maxwell first showed, there is a steady creep of gas across the plate from the colder edges to the hotter central region. The final behaviour of the radiometer depends greatly on the shape of the suspended vane. Its use is therefore restricted to qualitative investigation. On the other hand, *Knudsen's absolute manometer* rivals the McLeod gauge for the absolute determination of low pressures. It has the further advantage of measuring the pressures of vapours, but it is much less convenient to use.

* *Phys. Rev.*, Vol. 5, p. 213 (1915)

The instrument consists of two fixed mica strips heated electrically and placed on either side of a third strip suspended by a torsion wire. The radiometer forces exert a torque on the suspended strip, measurement being carried out with mirror, lamp and scale.

The torque is proportional to the gas pressure, and the theory of the instrument has already been discussed fully in this series.* The final relation obtained is

$$p = \frac{8\pi^2 \delta d_1}{D a t^2 d_2} \frac{T_2}{T_1 - T_2} \text{ dynes/sq. cm.,}$$

where d_1 is the scale deflection, d_2 the distance of the scale from the mirror, and a , t , δ and D are the area of one side, period of oscillation, moment of inertia, and mean diameter of the suspended strip respectively.† The range is from 10^{-2} mm. downwards, and the scale is linear except near the higher limit of pressure.

(c) Pirani-Hall gauge.

Since from equation (40), p. 207, the quantity of heat ΔQ conducted through a gas at low pressure is proportional to the pressure, a convenient gauge may be based on the change in electrical resistance of a heated tungsten wire immersed in the gas.

The general arrangement is shown in fig. 14, which shows a modification due to Hall and is self-explanatory. The gauge may be used in three ways: (1) the voltage may be maintained constant and the variation of the current i with the pressure p may be

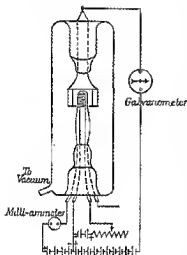


Fig. 15

observed, (2) the resistance may be maintained constant and the variation of energy input with p observed, or (3) the current may be maintained constant and the variation of r with p observed (Pirani-Hall method). Linear relations are obtained with different gases over a range of 10^{-2} mm. to 10^{-5} mm.; the apparatus is usually calibrated against the McLeod gauge.

(f) Ionization gauges.

These gauges are based on the dependence of ionization on gas pressure. The existence of a linear relation depends on the arrange-

* Roberts, *Heat and Thermodynamics*, fourth edition, p. 96 et seq.

† G. W. Todd, *Phil. Mag.*, Vol. 38, p. 381 (1919).

ment of the apparatus, a satisfactory form being that of Dushman and Pound shown in fig. 15.

The plate, which is in the form of a grid and occupies the position normally held by the latter in a triode, has a potential of about -1250 volts relative to the filament. The collector of the positive ions, which consists of an outer cylinder of molybdenum, has a potential of about -20 volts relative to the cathode. The positive ion current is registered by a sensitive galvanometer and is found to be linearly related to the gas pressure over a wide range. Experiments with argon, the pressure of which was determined simultaneously with a McLeod gauge, showed that the greater the electron current, the higher the pressure at which the linear relation remains valid. The range is from 10^{-6} mm. to the lowest pressures attainable.

In one modification of the ionization gauge, a magnetic field is applied so that the electrons move in long helical paths; they thus produce a maximum ionization by repeated collision with gas molecules, with a consequent increase in sensitivity of the instrument.

(g) *Effusion gauges.*

The use of effusion gauges is normally restricted to the measurement of vapour pressures of metals, an adequate account of which will be found in Roberts' *Heat and Thermodynamics*, fourth edition, p. 216 et seq.

(h) *Comparison of low-pressure manometers.*

The choice of a gauge for the measurement of high vacua depends on whether it is to be used to measure a steady pressure as accurately as possible, or whether it is required to indicate the presence of leaks in the vacuum system. Precise work will require many precautions whatever gauge is used and the final selection will depend very much on the individual experimental conditions. For leak-testing purposes the McLeod gauge is simple, reliable, and cheap, but it is bulky and not suitable for instantaneous readings. Its main disadvantage, however, is that any failure to keep the liquid air trap in full operation may lead to serious contamination by mercury vapour of metal parts of the system in general, and of the Apiezon oil pump in particular. The Pirani gauge has all the advantages of the McLeod gauge. In addition, readings can be taken at any distance from the apparatus, and they are instantaneous. It is, however, very sensitive to external and internal disturbances, such as mechanical shock and temperature fluctuation, the widely wandering zero which results makes detection of leaks with this instrument very difficult.

The ionization gauge is very sensitive, instantaneous, and flexible. Its disadvantage lies in the limited life of the filament, the high temperature of which will decompose organic and other vapours. Reliable results require regular degassing of the gauge which may prove tedious. While the Knudsen gauge may require great care when used

as an absolute instrument because of uncertainties connected with the accommodation coefficient, many workers consider it to be the best instrument for leak detection. For most thermal gauges the energy transfer due to molecular conduction and to radiation are comparable, but the momentum carried by the molecules greatly exceeds that of the photons. It is this fact that gives the Knudsen gauge an advantage over the Pirani gauge in freedom from external disturbances. Further advantages compared with other forms of manometer are the absence of a filament running at very high temperatures, and the absence of mercury vapour. However, the scale actually on the gauge must usually be read, and this may be a disadvantage since the gauge must be mounted close to the vacuum system.

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CHAPTER X

Osmotic Pressure

I. Osmotic Pressure of Solutions.

Various experiments lead to the view that in some way a substance in solution exerts a mechanical pressure on the walls of the containing vessel. To demonstrate this it is convenient to use a so-called semi-permeable membrane. This is a natural or artificial membrane, possessing the property of allowing the molecules of a solvent to pass through freely, but completely obstructing the molecules of a solute. For

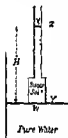


Fig 1

example, a gelatinous layer of cupric ferrocyanide, deposited in a porous pot, acts in this way with respect to a solution of cane sugar in water. It prevents the passage of the sugar, but freely transmits the water. A porous pot cylinder, with a semi-permeable membrane of cupric ferrocyanide deposited in its walls, is filled with a solution of cane sugar in water. A long glass tube is then fixed through the top of the cylinder, the joint is made watertight, and the cylinder is made to stand in a beaker of pure water. As time goes on, it is found that the liquid inside the glass tube rises to a considerable height and comes to rest

Fig 1 represents the situation after equilibrium has been reached. The cylinder has been adjusted so that the semi-permeable base just touches the pure water. Water has entered the cylinder and tube until the difference of the two levels has become H cm. A hydrostatic pressure of $g\rho H$ dynes per sq. cm., plus the pressure at X , now acts on the inner surface of the semi-permeable membrane in the base of the cylinder, where ρ is the density of the solution in its final state. A pressure $g\sigma H$, plus the pressure at X or Z , acts on the solvent at Y , where σ is the vapour density. The same pressure acts upwards on the lower side of the membrane. It may be said that a pressure $gH(\rho - \sigma)$, applied to the inner surface of the membrane or to the solution, prevents more water from entering. This quantity is called the *osmotic pressure* of the solution in its final state:

$$P = gH(\rho - \sigma). \quad \dots \dots \dots (1)$$

Semi-permeable membranes and the phenomenon of osmotic pressure play a great part in connexion with the properties of cells in plants and animals. Solutions with equal osmotic pressures, though not necessarily with the same solute or solvent, are said to be *isotonic*. In giving medical injections, swelling of the red blood corpuscles is avoided by using solutions isotonic with the contents of the corpuscles.

The osmotic pressure of a solution is often regarded as being produced in the same way as the pressure of a gas, that is, it is supposed that the molecules or ions of a solute are endowed with motion, that they bombard the walls of the containing vessel, and that the osmotic pressure is the normal momentum imparted to the walls per sq. cm. per sec. In dilute solutions it is supposed that the molecules or ions of the solute move about, unimpeded by the presence of the molecules of the solvent, and without exerting forces on one another; in fact, the solute behaves as a perfect gas would behave if it occupied the same total volume as the solution. Other views of osmotic pressure have been put forward from time to time, but these will not be considered here.

Experiment shows that the value of the osmotic pressure of a very dilute solution of a solute which does not dissociate when placed in the solvent is, in fact, that which it would have if the solute were a perfect gas occupying the same total volume as the solution. This result is known as *van't Hoff's law*, the classical law of osmotic pressure. In symbols, it may be written

$$\frac{PV}{M\theta} = \frac{R}{W}, \quad \dots \dots \dots (2)$$

where P is the osmotic pressure of the solution, V its volume, θ the absolute temperature, M the mass of solute, W the molecular weight of the solute, and R a constant. If P is in dynes per sq. cm., V in c.c., M in gm., and W the molecular weight, $R = 8.315 \times 10^7$. Its dimensions are those of work/temperature or $ML^2T^{-2}\theta^{-1}$. Equation (2) may also be written in the form

$$P = kn\theta, \quad \dots \dots \dots (3)$$

where k is Boltzmann's constant, equal to 1.372×10^{-16} , and n is the concentration of solute molecules in molecules per c.c. In the case of solutes where each molecule completely dissociates into ν ions, van't Hoff's law becomes

$$\frac{PV}{M\theta} = \frac{\nu R}{W}, \quad \dots \dots \dots (4)$$

which reduces to

$$P = \nu kn\theta. \quad \dots \dots \dots (5)$$

From another point of view, its efficiency is equal to the area of the cycle divided by the heat taken in by the substance along LM . The area of $LMNO$ = the area of $LMXY$ = $LYdV$. The quantity LY may be written in the form $(\partial P/\partial \theta)_v d\theta$, for it is the change in osmotic pressure at constant volume corresponding to a change of temperature $d\theta$. Hence the area is $(\partial P/\partial \theta)_v d\theta dV$. The solution is so dilute that along LM there is no heat of "further" dilution to allow for, and the only heat absorbed along LM by the solution is that required to make up for the work PdV done by the solution and so keep the temperature constant. The second expression for the efficiency becomes $\{(\partial P/\partial \theta)_v d\theta dV\}/PdV$. Equating the two expressions and clearing fractions, we have $(\partial P/\partial \theta)_v = P/\theta$. By integration,

$$\log P = \log \theta + \text{a constant,}$$

and

$$P = a\theta, \quad (6)$$

where a is a constant as far as temperature is concerned, but may depend on the volume. This result, of course, is part of van't Hoff's law.

3. Difference between the Vapour Pressure of a Pure Solvent and that of a Dilute Solution.

Consider the simple arrangement shown in fig. 1 and described on p. 234. Let the vapour pressures at points X and Y , just above the surfaces of solution and solvent, be p' and p respectively. Let the densities of the vapour and solution be σ and ρ . Neglect changes in vapour density with height. To get from X to Y , it is possible to proceed in two ways, (1) via the solution and solvent, along the route XWY , (2) via the vapour only, along the route XZY . The pressure change in going from X to Y must be the same along both paths. Along XWY , $p = p' + g\rho H - P$, since the pressure is p' at X , rises by $g\rho H$ in going from X to the bottom of the column of solution, and then falls by P as the semi-permeable membrane is crossed. Along XZY , $p = p' + g\sigma H$, since the drop in level in the vapour is the only cause of change in pressure. Hence $g\rho H - P = p - p' = g\sigma H$, $P = gH(\rho - \sigma)$, and $gH = P/(\rho - \sigma)$. Thus

$$p - p' = g\sigma H = \frac{P\sigma}{\rho - \sigma}. \quad (7)$$

Since $\sigma \ll \rho$, the approximation

$$p - p' = \frac{P\sigma}{\rho} \quad (8)$$

is often used.

4. Difference between the Boiling Point of a Pure Solvent and that of a Dilute Solution.

A liquid boils when its saturation vapour pressure is equal to the pressure of the atmosphere above its surface. Fig. 4 shows the curves connecting the saturation vapour pressure and the absolute temperature of a pure liquid and of a dilute solution with the same liquid as solvent. Let A represent the boiling point of the pure solvent at temperature θ . At this temperature the vapour pressure of the solution

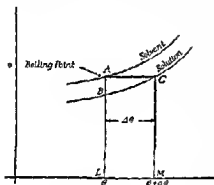


FIG. 4

is lower than that of the solvent, represented by the point B . To make the solution boil, its vapour pressure must be brought up to atmospheric pressure. This is done if the temperature is raised by an amount $\Delta\theta$, say, so that the vapour pressure p of the solution is represented by the point C , where $AL = CM = p$. Let $BL = p'$. The curve BC connects p' and θ . To a change in temperature $d\theta$, there corresponds a change of pressure $\bar{d}p'$. Hence to a

change in temperature $\Delta\theta$, there corresponds a change of pressure $(\bar{d}p'/d\theta)\Delta\theta$, which must be equal to $p - p'$. Thus

$$\Delta\theta = \frac{p - p'}{\bar{d}p'/d\theta}. \quad \dots \dots \dots (9)$$

Assume that the slopes of the two curves near A and B are equal, that is, that $dp/d\theta = \bar{d}p'/d\theta$, an assumption borne out by experiment. By a relation known as the first latent heat equation, or Clapeyron's equation,*

$$\frac{dp}{d\theta} = \frac{L}{\theta(v_2 - v_1)} \quad \dots \dots \dots (10)$$

during a change of state, where L is the latent heat in ergs per gramme, and v_2 and v_1 are the specific volumes of the vapour and liquid solvent respectively at temperature θ . Hence

$$\Delta\theta = \frac{p - p'}{L/\theta(v_2 - v_1)}. \quad \dots \dots \dots (11)$$

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 476

By equation (8),

$$p - p' = \frac{P\sigma}{\rho},$$

where σ is the vapour density of solvent vapour ($=1/v_2$), ρ the density of the dilute solution, and P its osmotic pressure. As the solution is dilute, assume that ρ is the density of the pure solvent. Then $\rho = 1/v_1$. In equation (11) substitute for $p - p'$ from equation (8), neglect v_1 in comparison with v_2 , since the specific volume of a liquid is so much less than that of its vapour, and replace v_2 by $1/\sigma$. Then

$$\Delta\theta = \frac{P\sigma/\rho}{L\sigma/\theta}$$

or

$$\Delta\theta = \frac{P\theta}{L\rho}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In numerical substitutions, P is in dynes per sq. cm., L in *ergs per gramme*, and ρ in grammes per c.c. $\Delta\theta$ is numerically positive, so that the solution has a higher boiling point than the solvent. Since $P = \nu kn\theta$, by equation (6),

$$\Delta\theta = \frac{\nu kn\theta^2}{L\rho}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

5. Difference between the Freezing Point of a Pure Solvent and that of a Dilute Solution.

The freezing point of a pure solvent is that temperature at which the liquid phase of the substance is in equilibrium with the solid phase and their vapour pressures are equal. If no substance other than the vapour occupies the space above the liquid and solid phases, all three phases, solid, liquid and vapour, can be in equilibrium, and the freezing point is also the triple point. If the vessel is open to the atmosphere, the freezing point is not quite the same as the triple point. For example, the ordinary melting point of ice is 0°C ., but the triple point is $+0.0074^\circ \text{C}$.

When a solution freezes, only the pure solvent crystallizes out. The freezing point is lower than that of the pure solvent, and is the temperature at which the solid phase of the solvent is in equilibrium with the liquid solution, that is, at which the vapour pressure of the solution is the same as that of the solid solvent. Consider fig. 5, in which AB represents the $p\theta$ curve of the vapour of the liquid solvent, DB represents that of the vapour of the solid solvent, and DC the $p'\theta$ curve of the vapour of the solution. B represents the freezing point and triple point of the pure solvent, D the freezing point of the solution.

Draw vertical straight lines ADH and BCK through D and B

A horizontal porcelain tube *A* (fig. 6) has a semi-permeable membrane of CuFe(CN)_6 deposited near the outer wall. The gun-metal case *B* enclosing *A* is filled with the solution under test by the side-tube *C*. The brass end-tubes *D* and *E* lead respectively to a vertical open graduated glass capillary tube and to a tap. The solvent (water) is placed in the porcelain, brass and glass tubes.

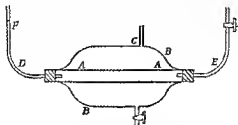


Fig. 6

Solvent tends to pass through the membrane, but is prevented by a hydrostatic pressure applied through *C*. When the applied hydrostatic pressure is just equal to the sum of the required osmotic pressure and the small hydrostatic pressure on the solvent in *A*, the meniscus in *F* remains stationary. The membrane was strong enough to allow osmotic pressures of 130 atmospheres to be measured.

A second arrangement for measuring osmotic pressure, suitable for concentrated solutions, is that of Frazer and Myrick, with improvements by Morse and Frazer, Grollman and Frazer, and Lotz and Frazer (see fig. 7). In order to stand pressures of the order of 250 atmospheres, a cylindrical earthenware cell *M*, of special quality, with a semi-permeable membrane of $\text{Cu}_2\text{Fe(CN)}_6$ inside its wall, is inserted in a bronze cylinder *J*. Pure solvent, e.g. water, is contained in the central space *L*, while the solution whose osmotic pressure is required is placed in the outer compartment *B* between *M* and *J*. A bent glass tube *T* serves to admit more solvent from outside and, being open to the atmosphere, the pressure at the meniscus level in the open arm has a known value. Leaks between cell and cylinder are avoided by using a washer *O* made of a substance known commercially in U.S.A. as "Rainbow Packing". In the older work the osmotic pressure itself was measured by connecting the top of the bronze cylinder *J* to a mercury-in-glass manometer. On account of several sources of error and the disadvantage of breaking at high pressure, the mercury manometer of older measurements is now replaced by a resistance manometer, i.e. in the upward prolongation of *J* a metal wire, suitably mounted, is included as part of an external electric circuit. As the hydrostatic pressure *P* on the wire increases, the electric resistance increases according to a linear law

$$R = a + bP \quad \text{or} \quad P = cR - d.$$

R is therefore measured and *P* calculated. This enables the work to be carried out for much higher pressures, i.e. with strong solutions.

There is still a source of error, namely hysteresis, i.e. a creep of the zero of the galvanometer used owing to a slow change of resistance, even when P is steady. Hence, in the latest form the pressure is measured by an optical method. The upward extension of J is made to form part of an optical interferometer, in which a beam of monochromatic light travels along a known length of the solution. Another

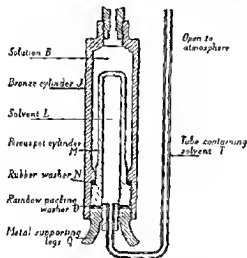


FIG 7

part of the same beam describes a similar path outside the solution, and the two parts are arranged to give interference fringes whose central fringe can be covered by the cross wire of an eyepiece. When the pressure on the solution increases, the refractive index also increases according to a linear law

$$\mu = a + bP \quad \text{or} \quad P = c\mu - d$$

The effective optical path of the light through the solution is increased,

(a) *Measurement of osmotic pressure by the method of isothermal distillation (see fig. 8).*

The method of isothermal distillation makes use of two general properties of liquids to which much attention is not usually given, viz

(1) that changing the hydrostatic pressure on the surface of a liquid changes its vapour pressure, and (2) that a column of de-aerated liquid can support the application of a longitudinal tension without breaking. It is a method suitable for smaller osmotic pressures, say, of not

more than one or two atmospheres.

In one and the same enclosure quantities of (a) pure solvent and (b) solution are exposed in separate containers. The vapour of the solvent fills the vessel above both the exposed surfaces. Since the vapour pressure of the solvent exceeds that of the solution, solvent at first distils over into the solution. The vapour pressure of the solvent is then reduced by making use of the two properties just mentioned, in that a normal tension is applied to the surface of the solvent, directed from the surface to the interior. This tension is simply the downward weight of a de-aerated column of solvent, hanging beneath the exposed surface. The length of the hanging column is adjusted until solvent ceases to distil over into the solution. It is then assumed that the vapour pressures of solvent and solution are equal. The osmotic pressure of the solution is then taken as equal to $g\rho h$, where ρ is the density and h the length of the suspended column.

In order to carry out the experiment the solvent is introduced into a porous disc made either of a mixture of clay (pot) and Pyrex glass powder (Townend) or a sintered glass filter plate (Ulmann). The pores are of such a size as to cause the solvent

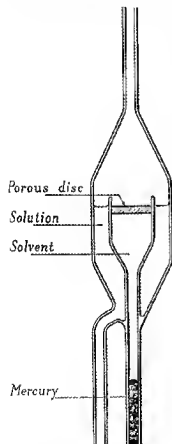


Fig. 8

surface, but are sufficiently small to ensure that the maximum capillary rise, if the pores were long enough, would be greater than the osmotic pressure to be measured. Underneath the porous disc, in contact with it and effectively hanging from it is a column of de-aerated solvent, and below that a column of mercury. This compound column is the one

which reduces the hydrostatic pressure on the surface of the solvent by an amount equal to the osmotic pressure to be measured. Instead of finding the equilibrium point by one tedious operation, it is determined by measuring the mass distilling over from solvent to solution per minute under various downward tensions.

A graph is plotted with masses distilling over per minute as ordinates and tensions per sq. cm. as abscissae. This graph is a straight line. The abscissa intercept for zero mass distilling over gives the tension per sq. cm. for that case, and this is the required osmotic pressure. Thermostatic temperature control is of very great importance, because a change in temperature of 0.00053°C . produces the same effect as an $N/1000$ solution. Air-free liquids are imperative. The concentration of the solution is determined at the end of an experiment from the refractive index, which is itself determined by an optical interferometer. The method has been successfully applied to organic solutions (Ulmann). The time taken by a measurement is said to be much shorter than by the clay-cell method.

(b) *The thermocouple method.*

In order to measure or compare the osmotic pressures of aqueous solutions available only in very small quantities down to about one milligramme, the method of Hall may be used, as modified by Baldes.

A thermocouple of the shape shown in fig. 9 is constructed with very thin wires of manganin and constantan. ABA represents constantan, AC (two pieces) represents manganin, and CD (two pieces) represents copper connecting wire. If the osmotic pressures of two solutions are being compared, a small drop of the first is pipetted on one junction A, and a similar drop of the second on the other junction. The pipetting is done in a humidified atmosphere, and the thermocouple is then immediately placed in a vessel whose inner walls are lined with moistened filter paper. Saturated water vapour from this filter paper fills the vessel. Condensation on both drops goes on.

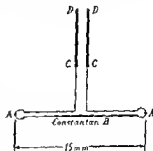


Fig. 9.—Comparison of osmotic pressures (Baldes' method)

Let p_1 , p_2 , and p_0 be the vapour pressures of the two solutions and the saturation vapour pressure of the water, respectively. The rate of condensation on the first junction is equal to $k(p_0 - p_1)$ grammes per second, where k is a constant. The latent heat of the condensed vapour warms the junction through $k'(p_0 - p_1)$ degrees C. The temperature of the junction then becomes constant, for the heat supplied by con-

densation is then equal to the heat lost by conduction, radiation, and convection. Similarly the temperature of the other junction rises to $k'(p_0 - p_2)$ degrees C. above its surroundings. A steady state is reached in which the temperature difference of the two junctions is equal to $k'(p_1 - p_2)$ degrees C., assuming that $p_1 > p_2$. An e.m.f. of value E volts is produced, and if t , the temperature difference, is very small, we have approximately

$$E = at.$$

Here

$$t = k'(p_1 - p_2),$$

hence

$$E = ak'(p_1 - p_2)$$

or

$$E = K(P_1 - P_2),$$

where P_1, P_2 , are the osmotic pressures and K is a constant of the instrument. This electromotive force E is measured. The constant K is found by calibrating with standard liquids of known vapour pressure.

Besides needing only small quantities, this method has the advantage of taking only a short time (of the order of several minutes) for the attainment of the steady state, whereas the clay-cell method takes days.

The accuracy of the present method is indicated by the fact that it measures values of $P_1 - P_2$ as low as 0.002 of the value of P_1 .

7. Raoult's Law.

Raoult's law asserts that when a solute is added to a solvent to form a dilute solution, the fractional drop in vapour pressure $(p - p')/p$ is equal to N_1/N_2 , where N_1 and N_2 , respectively, are the total numbers of solute and solvent molecules present (solute undissociated).

To prove this, replace $p - p'$ by $P\sigma/\rho = kn\theta\sigma/\rho$ by equations (8) and (3), where k is Boltzmann's constant, n the number of solute molecules per c.c., σ the vapour density, ρ the density of the solution (and of the solvent, approximately). Further, p , the saturation vapour pressure of the solvent, is given by the equation of state of a perfect gas, since the saturated state may be regarded as the last state to which the equation of state applies as the substance approaches condensation. Hence $p/\sigma = R\theta/W$, where W is the molecular weight of the solvent, and $p = R\theta\sigma/W$. We thus have $(p - p')/p = knW/R\rho$. Write $n = N_1/V$, where V is the volume of solution or solvent. Now ρ/W is the number of gramme-molecules of solvent per c.c., if ρ is regarded as the density of the solvent, $V\rho/W$ the total number of gramme-molecules of solvent present, and R/k the number of molecules in a gramme-molecule. Hence $V\rho R/Wk = N_2$, the number of actual molecules of solvent present. Then we have approximately

$$\frac{p - p'}{p} = \frac{N_1}{N_2}, \quad (15)$$

and $N_1/N_2 = n_1/n_2$, the ratio of the concentrations in molecules per c.c.

8. Two Classes of Electrolytes.

As far as aqueous solutions are concerned, there are two classes of electrolytes. The class of *weak electrolytes* includes those substances which when dissolved in water give solutions in which the process of dissociation into ions is far from complete. This statement holds even when the solutions are very dilute. In this class are many organic

moderately strong solutions. To this class belong most neutral salts and those acids and alkalis which have long been called "strong", for example, HCl , HNO_3 , H_2SO_4 , NaOH , KOH . The properties of solutions of weak electrolytes are well represented by the classical theory outlined on pp. 235-241, but this theory fails to explain the properties of solutions of strong electrolytes. Contributions to the theory of such solutions have been made by Sutherland, Bjerrum, Hertz, Milner, Ghosh and others, and especially by Debye and Hückel (1923 and onwards). As the theory of the last two authors is now generally accepted, an outline of the elementary part of it will be given here.

9. Modern Views of Osmotic Pressure.

The classical theory of the osmotic pressure of dilute solutions regards it as an effect of the same type as the pressure of gases, that is, the value of the osmotic pressure is calculated as the normal momentum imparted to the boundary surfaces per sq. cm. per sec. by the impact of the molecules or ions of the solute. It is assumed that no forces exist between the molecules or ions. Debye and Hückel's theory

These forces are given by Coulomb's law of inverse squares, and the solvent enters into the calculation because it fills the spaces between the ions and the value of its dielectric constant affects the value of the forces. Any given ion is more likely to be approached by ions of the opposite kind than by ions of the same kind. This affects the kinetic energy of the ions and reduces the osmotic pressure. In solutions of weak electrolytes the charged ions also exert forces on one another, but as they are relatively few in number compared with the total number of undissociated molecules present, the effect of the forces is relatively small, and weak electrolytes behave according to the classical theory.

10. Debye and Hückel's Theory of Strong Electrolytes.*

It is convenient to describe first the experimental results obtained with solutions of strong electrolytes. Suppose that the actual osmotic pressure of a solution is P , and that the osmotic pressure which the solution would have if it were completely dissociated into ions is P_0 . Write $P/P_0 = \beta$; β is called the *osmotic coefficient* of the solution, and is determined by experiments on the depression of the freezing point, &c. According to the classical theory of solutions,

$$1 - \beta = (\nu - 1)n^{\nu-1}/\nu K, \quad (16)$$

where n is the concentration of the electrolyte in molecules per c.c., ν the number of ions into which each molecule dissociates, and K the constant of equilibrium supposed to exist between molecules and ions, as given by the law of mass action (see Ex. 1, p. 316).

In the case of binary electrolytes like NaCl, $\nu = 2$ and $1 - \beta = n/2K$. A graph connecting $1 - \beta$ and n for such substances ought to be a straight line, beginning at the origin and making a finite angle θ with the axis of n , where $\tan \theta = 1/2K$. In other cases, when $\nu > 2$, the graph connecting $(1 - \beta)$ as ordinate and n as abscissa ought to be a curve starting at the origin with the axis of n as its tangent. The actual experimental results are in sharp contrast with these.

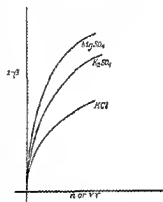


Fig. 10

(n is the concentration in grammes-molecules per litre of solution.)

Inspection of fig. 10 shows that in all cases the graph connecting $(1 - \beta)$ and the concentration n is a curve leaving the origin in such a way that the axis of $(1 - \beta)$ is a tangent to it. Thus the classical theory of osmotic pressure fails as regards strong electrolytes. It appears on closer examination that the states of such solutions are not governed by the classical law of mass action. Fig. 10 also shows that for a given concentration the value of $(1 - \beta)$ depends on the valency of the ions of the electrolyte concerned, that is, on the electric charges upon the ions. The classical theory fails in that it does not take into account the forces due to these electric charges. In the present exposition of Debye and Hückel's theory it is initially assumed that (1) the solutions under discussion have fairly low or low concentrations, (2) the electrolyte is completely dissociated into ions.

* Debye and Hückel, *Physikalische Zeits.*, Vol. 24, pp. 185, 305 (1923).

The classical value of the osmotic pressure P_o of a solution is $P_o = \nu nk\theta$, by equation (5). Let the actual osmotic pressure be P . It is required to express P in terms of P_o . Consider a volume V_o of a solution, enclosed in a cylindrical vessel provided with a piston of which the head is semi-permeable, that is, permeable to molecules of the solvent but impermeable to molecules of the solute. Let there be pure solvent behind the piston head. Consider the work which must be done by an external agent, who may be called the operator, to obtain V c.c. of solution, starting with pure solvent, working at constant temperature and by purely reversible processes. Two convenient ways of effecting this change offer themselves, and, by a property of the quantity known as the available energy of a system, or otherwise, it may be shown that the work done by the operator is the same in each case.

First of all, the solution may be compressed infinitely slowly from the state of zero concentration (infinite dilution) and volume V_o to the final volume V . The total work done by the operator in this process is $-\int_{V_o}^V P dV$ ergs $= W_1$, say. Note that in the usual notation of thermodynamics, $\partial W_1 / \partial V = -P$. Secondly, the operator may start with a solution of zero concentration, regarding it as containing ions infinitely far apart, and take away the charges from the ions infinitely slowly. Then the solution may be compressed from a state of zero concentration and volume V_o to the final volume V , the charges on the ions being absent. The charges may then be restored to the ions infinitely slowly. In this way the solution reaches the same final state as before. During the compression, the work done by the operator is $-\int_{V_o}^V P_o dV = W_2$, say, where P_o represents the osmotic pressure calculated by classical reasoning, since electric charges are absent. Hence $\partial W_2 / \partial V = -P_o$. Let the work done by the operator in removing and restoring the electric charges be W_3 . Then since the total work done by the operator is the same in the two processes,

$$W_1 = W_2 + W_3 \quad \dots \quad (17)$$

Differentiate with respect to V , keeping the temperature constant. This gives

$$\frac{\partial W_1}{\partial V} = \frac{\partial W_2}{\partial V} + \frac{\partial W_3}{\partial V},$$

or

$$-P = -P_o + \frac{\partial W_3}{\partial V}.$$

Hence

$$P = P_o - \frac{\partial W_3}{\partial V} \quad \dots \quad (18)$$

Thus the question of finding P in terms of P_0 is reduced to the problem of finding $\partial W_{el}/\partial V$. The quantity W_{el} consists of two parts, (a) the work w_1 done by the operator in removing the charges from the ions when the ions are infinitely far apart, (b) the work w_2 done by the operator in restoring the charges after the final concentration has been reached. If we regard the ions as spheres, each of radius b cm., charge e e.s.u., infinitely far apart, and immersed in a solvent of dielectric constant D e.s.u., the energy of each ion, regarded as a charged condenser of capacity Db e.s.u., is $e^2/2Db$ ergs. It is this energy which is allowed to return to infinity when the ions are discharged. Thus the work done by the operator per ion is $-e^2/2Db$ ergs. If in V c.c. of solution there are N ions of each kind, the total work is

$$w_1 = -\frac{Ne^2}{Db} \text{ ergs.} \quad \dots \dots (19a)$$

In calculating w_2 , the work of restoring the charges to the ions at finite concentration, we must take account of the work done in bringing up a charge to each ion against the mean potential due to other ions, as well as against its own potential. Thus w_2 consists of two parts, which we shall call w_3 and w_4 respectively. The work done against an ion's own potential, by a similar calculation to that just carried out, is equal to $+e^2/2D'b$ ergs per ion, where D' represents the effective dielectric constant of the medium around an ion.

For the N ions of each kind in V c.c. of solution, the total work

$$w_3 = \frac{Ne^2}{D'b} \quad \dots \dots (19b)$$

In strong solutions $D' \neq D$, on account of the proximity of other ions, although in dilute solutions D and D' may be assumed to be equal.

The work w_4 done against the mean potential due to other ions is much greater than either of the quantities of work just calculated, and requires detailed consideration. Assume that the aqueous solution under discussion contains a single binary monovalent electrolyte such as NaCl or KCl, whose ions carry charges $+e$ and $-e$ respectively, where e is 4.774×10^{-10} e.s.u. We now calculate the mean electrostatic potential which the neighbouring ions produce at a point which is about to be occupied by the centre of a given ion. Let there be n ions of each kind per c.c. The number of negative ions surrounding a given positive ion, when averaged over a certain time, exceeds the number of positive ions, because of the attraction of unlike charges. The excess is affected by temperature changes. Let ϕ be the as yet uncalculated resultant potential at a point at a definite distance from the centre of a selected positive ion and outside it, due to that selected ion and to the rest of the ions. To bring a charge $+e$ there, work $e\phi$

ergs must be done by the operator, and $-e\phi$ ergs are required to bring a charge $-e$ there. We now apply the Maxwell-Boltzmann theorem* to calculate the average concentration (in time) of ions of each sort in an element of volume dV near the point in question. According to that theorem, the number of positive ions in this element is $Ae^{-e\phi/k\theta} dV$, where k is Boltzmann's constant, and e is the base of Napierian logarithms. A is a constant which is equal to n , since the expression must hold when $\theta = \infty$, a temperature at which we may assume that the ions are uniformly distributed, with a concentration n of each kind per c.c., and $Ae^0 dV = AdV = ndV$. Similarly, the number of negative ions in the element dV is $ne^{+e\phi/k\theta} dV$. Since the ionic charges are $+e$ and $-e$ respectively, the net amount of positive charge in the element dV is $ne\{e^{-e\phi/k\theta} - e^{+e\phi/k\theta}\} dV$, that is,

$$ne\{e^{-e\phi/k\theta} - e^{+e\phi/k\theta}\} \text{ e.s.u. per c.c.} = \rho, \text{ say.} \quad (20)$$

As this is a problem in electrostatics, Gauss's theorem holds. Apply it to the element dV , which may be regarded as a rectangular parallelepiped. This gives Poisson's equation,

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = -\frac{4\pi\rho}{D}, \quad (21)$$

which may be written in the shorter form

$$\Delta\phi = -\frac{4\pi\rho}{D}. \quad (22)$$

In this equation substitute the value of ρ from equation (20). Then

$$\Delta\phi = \frac{4\pi ne}{D} (e^{+e\phi/k\theta} - e^{-e\phi/k\theta}) \quad (23)$$

Assume that the electrical energy $e\phi$ is small compared with the mean kinetic energy $k\theta$ due to thermal agitation. The exponentials can then be expanded in series of terms in $e\phi/k\theta$, so that, neglecting terms in ϕ of degree higher than the first, we get

$$\Delta\phi = \frac{8\pi ne^2 \phi}{Dk\theta}, \text{ approximately.} \quad (24)$$

This may be written in the form $\Delta\phi = x^2 \phi$, where $x^2 = 8\pi ne^2 / Dk\theta$. Debye and Hückel call $1/x$, which has the dimensions of a length, the characteristic length of the solution.

When Poisson's equation is expressed in polar co-ordinates, and

* Jeans, *Dynamical Theory of Gases*, 2nd ed., equation (936) (Cambridge University Press, 1921)

when the element of volume dV has the form of a spherical shell contained between spheres of radii r and $r + dr$, the equation becomes

$$\frac{1}{r^2} \left(\frac{d(r^2 d\phi/dr)}{dr} \right) = \frac{8\pi n e^2 \phi}{Dk\theta} \quad \dots \dots \dots (25)$$

$$= x^2 \phi. \quad \dots \dots \dots (26)$$

This type of element has the advantage of spherical symmetry. One general solution of equation (26) is

$$\phi = \frac{Ae^{-xr}}{r} + \frac{Be^{+xr}}{r}. \quad \dots \dots \dots (27)$$

Since $\phi = 0$ when $r = \infty$, this reduces to

$$\phi = \frac{Ae^{-xr}}{r}. \quad \dots \dots \dots (28)$$

This is the potential at a point outside the selected ion. Now in aqueous solutions it may be shown that each ion carries with it a layer of surrounding water molecules, which increases its effective size. Assume that each such ion is effectively a sphere of radius a cm.,* of which the interior is a medium of dielectric constant D , with a point charge $+e$ or $-e$ at the centre. Assume that the potential at any point inside this sphere is

$$\phi' = \frac{e}{Dr} + B, \quad \dots \dots \dots (29)$$

where B is a constant to be determined. At the boundary of the sphere of radius a , two conditions must be fulfilled. For $r = a$, $\phi = \phi'$, and also for $r = a$, $\partial\phi/\partial r = \partial\phi'/\partial r$. From the first condition,

$$\frac{Ae^{-xa}}{a} = \frac{e}{Da} + B. \quad \dots \dots \dots (30)$$

From the second,

$$Ae^{-xa} \frac{(1+xa)}{a^2} = \frac{e}{Da^2} \quad \dots \dots \dots (31)$$

From equations (30) and (31),

$$A = \frac{e e^{-xa}}{D(1+xa)} \quad \dots \dots \dots (32)$$

and

$$B = - \frac{ex}{D(1+xa)} \quad \dots \dots \dots (33)$$

The value of B represents the potential which the surrounding ions produce at the centre of the given ion. e/Dr is the potential at any

*The quantity a represents the average value of the shortest distance between the centres of the selected ion and other ions of both kinds. The quantity b of p. 249 is the radius of the actual ion, and $b \ll a$.

internal point due to the ion's own charge. When α is small compared with unity, that is, when α is small and the concentration is small, the value of B , namely, $-\alpha x/D(1 + \alpha x)$, reduces to

$$B = -\frac{\alpha x}{D} \quad \dots \quad (34)$$

The further discussion is limited to this case.

It is now necessary to find the work required to bring up a charge $+e$, in elements each of value dx , from infinity to a point where there is a potential due to other charges of value $B = -\alpha x/D$. (This process is a purely mathematical device, since actually the charge can assist only as a multiple of the electronic charge.) The element of work done in bringing a charge $+de$ to the point is

$$Bde = -\frac{\alpha x de}{D} \quad \dots \quad (35)$$

Substitute the value of x given by equation (24) in (35). This gives

$$Bde = -\left(\frac{8\pi n}{Dk\theta}\right)^{\frac{1}{2}} \frac{e^2 ds}{D},$$

and by integration the total work done in bringing up $+e$ is $-(8\pi n/Dk\theta)^{\frac{1}{2}} e^2/3D$ ergs, that is, $-e^2\alpha/3D$ ergs per ion, since $\alpha = (8\pi ne^2/Dk\theta)^{\frac{1}{2}}$ by equation (24). If in the solution of volume V c.c. there are N ions of each kind, the total work done in bringing up their charges against the potentials of the surrounding ions is

$$w_2 = -\frac{2Ne^2\alpha}{3D} \text{ ergs} \quad \dots \quad (36)$$

This is a negative quantity. It is far greater numerically than w_1 or w_3 , where $w_1 = -Ne^2/Db$ and $w_3 = Ne^2/D'b$ as given by equations (19a) and (19b), respectively, for dilute solutions, since D and D' are nearly equal. Hence the quantity W_s of equation (17) $= w_1 + w_2 = w_1 + w_2 + w_3 = w_3$ approximately. That is,

$$W_s = -\frac{2Ne^2\alpha}{3D} \text{ ergs}, \quad \dots \quad (37)$$

and, on substituting $\alpha = (8\pi ne^2/Dk\theta)^{\frac{1}{2}}$ and $n = N/V$, we have

$$W_s = -2Ne^2 \frac{(8\pi Ne^2/V D k \theta)^{\frac{1}{2}}}{3D} \quad \dots \quad (38)$$

Hence

$$\frac{\partial W_s}{\partial V} = Ne^2 \frac{(8\pi Ne^2/D k \theta)^{\frac{1}{2}}}{3DV^{\frac{3}{2}}},$$

if we keep N constant during the differentiation, or

$$\frac{\partial W_z}{\partial V} = \frac{e^2 x N}{3DV}.$$

Equation (18) becomes

$$P = P_a - \frac{e^2 x N}{3DV}. \quad \dots \dots \dots (39)$$

For an aqueous solution of a binary salt of the type considered, the classical value of the osmotic pressure is $P_a = \nu n k \theta = 2n k \theta$. Hence

$$P = 2n k \theta \left(1 - \frac{e^2 x}{6Dk\theta} \right). \quad \dots \dots \dots (40)$$

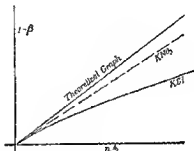


Fig. 11

Now the osmotic coefficient

$$\beta = \frac{P}{P_a} = 1 - \frac{e^2 x}{6Dk\theta}, \quad \dots \dots \dots (41)$$

and

$$1 - \beta = \left(\frac{P_a - P}{P_a} \right) = \frac{e^2 x}{6Dk\theta}. \quad \dots \dots \dots (42)$$

Since

$$x \propto n^{\frac{1}{2}}, \quad 1 - \beta \propto n^{\frac{1}{2}}. \quad \dots \dots \dots (43)$$

This relation agrees well with experiment for solutions of low concentration (see fig. 11).

11. Solutions of Strong Electrolytes of any Type.

Consider an aqueous solution of a single strong electrolyte, each of whose molecules splits up into $\nu_1, \nu_2, \dots, \nu_i$ ions of types 1, 2, \dots, i respectively, with valencies z_1, z_2, \dots, z_i respectively. Let n be the concentration of molecules per c.c. Then the concentrations of the ions are $n\nu_1, n\nu_2, \dots, n\nu_i$ respectively. In this case, when Boltzmann's

theorem is applied as on p. 250, the number of ions of class i in an element of volume dV is found to be $n\nu_i e^{-z_i e \phi / k\theta} dV$, and their contribution to the total charge per c.c. is $z_i e n \nu_i e^{-z_i e \phi / k\theta}$. If, as before, we assume that the index is small and expand the exponential to two terms, this charge becomes $+n z_i \nu_i e (1 - z_i e \phi / k\theta)$ approximately, and the total charge per c.c. due to all classes of ions is

$$\rho = \sum n z_i \nu_i e \left(1 - \frac{z_i e \phi}{k\theta} \right) \text{ approximately.} \quad (44)$$

Now an undissociated molecule is electrically uncharged. Hence $\sum z_i \nu_i e = 0$, for it is the sum of the charges on the ions arising out of a single molecule. Hence, expanding the expression for ρ , we find that $\rho = \sum n z_i \nu_i e - n e^2 \phi \sum \nu_i z_i^2 / k\theta$ is given by the second term only, that is,

$$\rho = - \frac{n e^2 \phi \sum \nu_i z_i^2}{k\theta} \quad (45)$$

Poisson's equation $\Delta \phi = -4\pi \rho / D$ becomes

$$\Delta \phi = \frac{4\pi n e^2 \phi \sum \nu_i z_i^2}{D k \theta} \quad (46)$$

or

$$\Delta \phi = x^2 \phi, \quad (47)$$

where

$$x^2 = \frac{4\pi n e^2 \sum \nu_i z_i^2}{D k \theta}. \quad (48)$$

The further steps in the theory are the same as for solutions of binary salts. As before, the solution of equation (47), expressed in polar co-ordinates, is

$$\phi = \frac{A e^{-x r}}{r} \quad (49)$$

outside the ion. If an ion is supposed to be a sphere of radius a_i cm., with a charge $z_i e$ at the centre, the sphere being composed of a medium of dielectric constant D , then the internal potential at any point may be supposed to be

$$\phi' = \frac{z_i e}{D r} + B \quad (50)$$

B is that part of the internal potential contributed by external ions, and $z_i e / D r$ is that part of the internal potential contributed by the ion itself. At the surface of the sphere there must be continuity of field and potential, that is, when $r = a_i$, $\phi = \phi'$ and $\partial \phi / \partial r = \partial \phi' / \partial r$.

After substituting the values of ϕ and ϕ' derived from equations (49) and (50), in these boundary equations, we find that

$$A = \frac{z_i e \epsilon^{x a_i}}{D(1 + x a_i)} \quad . \quad . \quad . \quad (51)$$

and

$$B = - \frac{z_i e x}{D(1 + x a_i)} \quad . \quad . \quad . \quad (52)$$

For dilute solutions,

$$x a_i \ll 1 \quad \text{and} \quad B = - \frac{z_i e x}{D} \quad . \quad . \quad . \quad (53)$$

As in the case of solutions of binary salts, the work required to bring a charge up to a point against the potential of surrounding ions is the most important part of W_x (see p. 252), and the other quantities of work done in discharging the ions at zero concentration and in charging the ions against their own potential are neglected in comparison with this. To bring up a charge $z_i e$ in elements, each of value $z_i d\epsilon$, from infinity to a point where the potential is B , the work required is $\int_0^x B z_i d\epsilon$, that is, by equation (53), $-\int_0^x z_i^2 e x d\epsilon / D$. The quantity x can be written in the form $x = C\epsilon$, where C does not contain ϵ , by equation (48). After substituting and integrating, we find that the work required is $-C z_i^2 e^3 / 3D$ ergs $= -z_i^2 e^2 x / 3D$. There are ν_i ions of this kind per molecule, so that the work required to bring up all their charges is $-\nu_i z_i^2 e^2 x / 3D$ ergs. Hence W_x , the total work for all the ions of all kinds in N molecules, is given by

$$W_x = - \frac{N e^2 x (\sum \nu_i z_i^2)}{3D} \text{ ergs.} \quad . \quad . \quad . \quad (54)$$

As before, by equation (18), $P = P_s - \partial W_x / \partial V$, where V is the total volume of solution. V enters into the expression for W_x in the factor $x = \{4\pi n e^2 (\sum \nu_i z_i^2) / D k \theta\}^{\frac{1}{2}}$ by equation (48). In fact, $n = N/V$ and $W_x = -F n^{\frac{1}{2}} = -F N^{\frac{1}{2}} / V^{\frac{1}{2}}$, where F is a factor which does not contain n or V . Hence $\partial W_x / \partial V = F N^{\frac{1}{2}} / 2 V^{\frac{3}{2}} = -W_x / 2V$. If in this we substitute the full expression for x , equation (18) can be written in the form

$$P = P_s - N e^2 \left\{ 4\pi n e^2 \frac{\sum \nu_i z_i^2}{D k \theta} \right\}^{\frac{1}{2}} \frac{\sum \nu_i z_i^2}{6 D V} \quad . \quad . \quad (55)$$

Write $P_s = (n \sum \nu_i) k \theta$, for $n \sum \nu_i$ is the number of ions per c.c. Then

$$P = (n \sum \nu_i) k \theta \left[1 - N e^2 \left\{ 4\pi n e^2 \frac{\sum \nu_i z_i^2}{D k \theta} \right\}^{\frac{1}{2}} \frac{\sum \nu_i z_i^2}{6 D V k \theta n \sum \nu_i} \right].$$

Now the osmotic coefficient $\beta = P/P_n$ and $N = Vn$. Hence

$$1 - \beta = \frac{P_n - P}{P_n} = c^2 \left\{ 4\pi n c^2 \frac{\sum v_i z_i^2}{Dk\theta} \right\}^{\frac{1}{2}} \frac{\sum v_i z_i^2}{6Dk\theta \sum v_i}.$$

Write $\sum v_i = \nu$ and $n = \gamma \times 6.06 \times 10^{23}/1000 = \gamma N_s/1000$, where γ is the concentration in gramme-molecules per litre, and N_s is the number of actual molecules in a gramme-molecule. Then $(1 - \beta)$ may be written in the form given by Debye and Huckel, namely,

$$1 - \beta = c^2 \left\{ \frac{4\pi N_s c^2}{1000 Dk\theta} \right\}^{\frac{1}{2}} \left\{ \frac{\sum v_i z_i^2}{\nu} \right\}^{\frac{1}{2}} \frac{(\gamma \nu)^{\frac{1}{2}}}{6Dk\theta}. \quad (56)$$

Comments.—(1) This expression shows that $(1 - \beta)$, with small concentrations, depends on the number and valency of the ions, as represented by $\sum v_i z_i^2$, on the nature of the solvent, as represented by D , and on the temperature θ .

(2) $(1 - \beta)$ is proportional to $(\gamma \nu)^{\frac{1}{2}}$.

(3) The expression $(\sum v_i z_i^2 / \nu)^{\frac{1}{2}}$ is called the *valency factor* and may be denoted by ν .

(4) For dilute aqueous solutions at ordinary temperatures, $D = 83.23$ and $(1 - \beta) = 0.263z(\gamma \nu)^{\frac{1}{2}}$.

(5) For KCl, $\nu = 1$; for K_2SO_4 , $\nu = 2\sqrt{2}$; for $La(NO_3)_3$, $\nu = 3\sqrt{3}$, and for $MgSO_4$, $\nu = 4\sqrt{4} = 8$.

(6) Fig. 12 shows graphs connecting $(1 - \beta)$ and $(\gamma \nu)^{\frac{1}{2}}$. Curves derived from experiment and from the above theory agree well at low concentrations, but an increasing divergence appears as the concentration is increased. The experimental values of β were obtained by determining the depression of the freezing point in each case.

(7) Equation (18), which is derived from thermodynamics, is true no matter what detailed theory of osmotic pressure may be adopted.

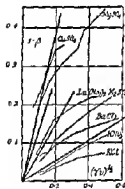


FIG. 12

12. More Exact Theory.

If in the equation $B = -z_+ z_- / D(1 + z_+ z_-)$ on p. 255, $z_+ z_-$ is not very small compared with unity, that is, if the solution is not assumed to be very dilute, the theoretical results and the graph agree well with those derived from experiment up to much higher concentrations. Space will not permit a full account of the theory*. It will suffice to quote the result for a aqueous solution, namely,

$$1 - \beta = 0.263z(\gamma \nu)^{\frac{1}{2}} f(z_+ z_-), \quad (57)$$

where α is the mean value of all the quantities α_i ; $f(z_+ z_-)$ is a function of $z_+ z_-$, namely

$$f(z_+ z_-) = 1 - \frac{3z_+ z_-}{2} + \frac{8z_+^2 z_-^2}{5} - 2z_+^3 z_-^3 + \dots \quad (58)$$

The other symbols have the same meaning as in section 11.

To apply equation (57), Debye and Huckel take as the mean ionic radius α that value of α which makes the theoretical value of $1 - \beta$ for the highest con-

* See Debye and Huckel, *Physikalische Zeits.*, Vol. 24, pp. 185, 306 (1923).

centrations coincide with the experimental value. It is then found that there is very good agreement at lower concentrations (fig. 13). The value of the mean radius a for KCl solutions is 3.76×10^{-8} cm.

Even with the more general theory just given, various discrepancies between experiment and theory still persist. When the mean ionic radii of the alkali chlorides, calculated from the above theory, are examined, it appears that LiCl has the greatest diameter, NaCl the next, and so on to CsCl, which has the least. From the X-ray examination of crystals, however, it appears that LiCl has the smallest diameter, in contradiction to the above. At very high concentrations, moreover, the value of $1 - \beta$ for LiCl decreases as γv is increased. Finally $1 - \beta$ changes sign, so that β becomes greater than unity, and the osmotic pressure P exceeds the classical value P_s . To explain these and other points it is necessary to take into account the deformability of the ions in strong fields and the presence of dipoles in the molecules of the solvent.

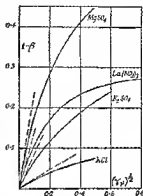


Fig. 13

CHAPTER XI

Diffusion

1. Diffusion in Liquids.

The diffusion or wandering of the molecules or ions of a solute in a solution * from a region of high concentration to a region of low concentration is called diffusion.

the behaviour of one particular ion but to the general effect, it is irreversible. A portion of a pure solvent, having once become impregnated with a solute, never again rids itself of the solute, unless aided by some external agent. Although in the case of strong electrolytes the molecules are completely dissociated and the ions move about separately, yet from the macroscopic point of view it is usual to consider the diffusion of the solute as if its molecules remained undissociated. For example, chemical analysis of a portion of a liquid taken from a particular region gives the concentration of the solute there.

The quantitative treatment of the phenomenon is based upon Fick's law of diffusion, which is analogous to Fourier's law of conduction of heat and to Ohm's law of conduction of electricity, all governing processes which in a certain sense are irreversible. Fick's law may be stated thus:

$$Q = -DA \frac{dn}{dx}, \quad (1)$$

where Q is the mass of a solute in grammes carried across an area A sq. cm. of a surface normal to the direction of diffusion in one second, n is the concentration of solute in grammes per c.c. at a point x cm. distant from some arbitrary origin, and $-dn/dx$ is the gradient or rate of decrease of concentration per cm. in the direction of diffusion. D is a quantity called the *coefficient of diffusion* or the *diffusivity* of the solute in a solution of concentration n . It is found that the value of D depends on that of n , so that the diffusivity of a given solute in a given solvent is not constant, but a function of n . As an example of a recent accurate determination of D , an account of Furth and Zuber's method will be given.

* For a brief discussion of diffusion of gases, see Chap. IX, p. 199.

2. Measurement of the Diffusivity of a Solute in a Liquid. Fürth and Zuber's Method.

Theory. The differential equations.

Let a solute diffuse along a cylindrical column of liquid bounded laterally by impervious walls. Consider the mass of solute accumulating per second within a thin transverse slice of the column, whose faces have co-ordinates x and $x + dx$. For this purpose we take into account (a) the solute diffusing into the slice across the first face, and (b) the solute diffusing out of the slice across the second face. As the lateral walls are impenetrable these two processes are the only processes affecting the mass accumulating within. By Fick's law, the mass of solute entering the slice across the first face, per second, is, by equation (1)

$$Q_1 = -DA \frac{\partial n}{\partial x} \quad \dots \dots \dots (2)$$

By the same law the mass of solute diffusing out of the slice across the second face, whose co-ordinate is $x + dx$, is the same function of $x + dx$ as Q_1 is of x . Hence, by Taylor's theorem, it is equal to $Q_1 + dx (\partial Q_1 / \partial x)$ plus negligible terms, since the slice is thin. On subtracting what diffuses out from what diffuses in, we find the resultant mass accumulating within the slice per second to be

$$-dx \frac{\partial Q_1}{\partial x} = DA \frac{\partial^2 n}{\partial x^2} dx, \quad \dots \dots \dots (3)$$

when D is independent of n , the concentration. If, however, D is dependent on n , the equation (3) must be replaced by

$$-dx \frac{\partial Q_1}{\partial x} = A \frac{\partial}{\partial x} \left(D \frac{\partial n}{\partial x} \right) dx. \quad \dots \dots \dots (4)$$

It turns out, by experiment, that D is only independent of n in very dilute solutions.

From the point of view of increase of mass with time, since the mass of solute within the slice is the concentration multiplied by the volume, i.e. is equal to $nAdx$ grammes, the rate of increase of this mass per second is $A \cdot dx \cdot \partial n / \partial t$, where t is the time in seconds. On equating the two values of the same thing, we get

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \quad \dots \dots \dots (5)$$

as the differential equation representing the diffusion phenomenon in the case of constant D . The student will note the analogy of diffusion

problems with those of thermal conduction, and, in particular, that equation (5) is analogous to the equation

$$\frac{\partial T}{\partial t} = \frac{K}{\rho s} \frac{\partial^2 T}{\partial x^2} \quad \dots \quad (6)$$

representing the conduction of heat along a lagged bar. Here T is the temperature, K is the thermal conductivity, ρ the density, and s the specific heat of the material of the bar. The analogy also suggests why $K/\rho s$ is called the thermal diffusivity. When D depends on the concentration, (5) is replaced by

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial n}{\partial x} \right) \quad \dots \quad (7)$$

Case I. D independent of the concentration n .

Furth and Zuber's method of measuring the diffusivity D makes use of a solution of equation (5) appropriate to the following experimental circumstances.

The lower half of a rectangular glass vessel is occupied initially by a solution of uniform concentration n_0 , and the upper half by a quantity of the pure solvent, the two being separated by a thin horizontal plane sliding screen. The central horizontal plane of the vessel which is the plane of the slider is $x = 0$, and x is to be measured upwards. At time $t = 0$ the slider is gently removed and diffusion commences. What is the value of the concentration n at any height x above the central plane at any subsequent moment t ? We shall restrict the discussion to places with values of x which are small compared with $2l$, the total height of liquid in the vessel. This is done by putting l equal to infinity at a certain point in the analysis. The experimental measurements are based on this theory.

Our next step is to find a solution of equation (5) satisfying these experimental conditions. First let $-x/t^{1/2} = s$ and try the solution

$$n = f(s) = f(-x/t^{1/2}). \quad \dots \quad (8)$$

On substituting this in the differential equation (5) we get

$$-f''(s) \cdot x/2t^{3/2} = D \cdot f''(s)/t. \quad \dots \quad (9)$$

Write $f'(s) = v$ and $f''(s) = dv/ds$. (10)

Then, we get $dv/v = -s ds/2D$ (11)

After integrating, this becomes

$$\log v = -s^2/4D + \text{constant}, \quad \dots \quad (12)$$

$$v = f'(s) = Ce^{-s^2/4D}. \quad \dots \quad (13)$$

$$\text{Hence} \quad n = f(s) = \int_0^s f'(s) ds = C \int_0^s e^{-s^2/4D} ds. \quad (14)$$

$$\text{Next write} \quad s^2/4D = x^2/4Dt = y^2, \quad (15)$$

$$\text{i.e.} \quad y = x/2(Dt)^{1/2} = s/2D^{1/2}, \quad dy = ds/2D^{1/2}. \quad (16)$$

$$\text{Hence} \quad n = 2D^{1/2}C \int_0^y e^{-y^2} dy = B \int_0^y e^{-y^2} dy \quad (17)$$

is a solution, where B is a constant, whose value is yet to be found. Hence also

$$n = B_0 + B \int_0^y e^{-y^2} dy, \quad (18)$$

where B_0 is a constant, is also a solution of equation (6). Our solution must satisfy, first, the initial condition that when $t = 0$, $n = 0$ everywhere over the range $0 < x < +l$, where $2l$ is the total depth of liquid. As already mentioned, we shall only work with values of x which are very small compared with l , and so we shall replace the range $0 < x < +l$ by $0 < x < +\infty$. Now

$$\int_0^\infty e^{-y^2} dy = \frac{1}{2}\pi^{1/2}. \quad (19)$$

Hence, on applying the initial condition, we get

$$0 = B_0 + \frac{1}{2}B\pi^{1/2}. \quad (20)$$

Next apply the condition that after an infinite time $t = \infty$, the concentration is uniform throughout the liquid and equal to $\frac{1}{2}n_0$, half the original concentration in the lower half. In this case the upper limit of the integral and therefore the integral itself are zero. Hence

$$\frac{1}{2}n_0 = B_0 + 0. \quad (21)$$

$$\text{Hence} \quad B_0 = \frac{1}{2}n_0 \quad \text{and} \quad B = -n_0/\pi^{1/2}. \quad (22)$$

Hence our solution, applying to all points in the upper half of the liquid, is

$$n = \frac{1}{2}n_0 - n_0 \int_0^y e^{-y^2} dy / \pi^{1/2} \quad (23)$$

$$= \frac{1}{2}n_0 \left\{ 1 - 2 \int_0^y e^{-y^2} dy / \pi^{1/2} \right\}, \quad (24)$$

$$\text{where} \quad y = x/2(Dt)^{1/2} \quad \text{or} \quad y^2 = x^2/4Dt. \quad (25)$$

$$\text{Hence} \quad 1 - 2n/n_0 = 2 \int_0^y e^{-y^2} dy / \pi^{1/2} = f_1(y), \text{ say.} \quad (26)$$

Tables of values of the Gaussian integral (error function) $\int_0^y e^{-y'^2} dy'$ are generally available and hence values of $2 \int_0^y e^{-y'^2} dy'/\pi^{1/2} = f_1(y)$ can easily be calculated for various values of y .

These results can be regarded from the converse point of view, i.e. given values of $f_1(y)$, the value of y can be found. This is exactly what is done. Experiments about to be described give numerical values of n and n_0 so that the quantity $1 - 2n/n_0 = f_1(y)$ is known. Then, using the converse point of view just mentioned, y is found. Now

$$y^2 = x^2/4Dt,$$

hence

$$D = x^2/4ty^2, \quad . \quad . \quad (27)$$

and numerical values of D are calculated.

Case II. D dependent on the concentration n .

In this case equation (7) holds:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial n}{\partial x} \right)$$

Again write $s = x/t^{1/2}$ and try the solution

$$n = f(s) = f(x/t^{1/2}),$$

where $f(s)$ means some as yet unknown function of s . On substituting in (7) we get

$$-f'(s) \cdot x/2t^{3/2} = \frac{\partial}{\partial x} (D \cdot f'(s)/t^{1/2}),$$

$$\text{which becomes} \quad -f'(s) \cdot s/2t^{1/2} = \frac{\partial}{\partial x} (D \cdot f'(s)), \quad (28)$$

and, on writing $dn/ds = f'(s) = v$, we get

$$-vs/2t^{1/2} = \frac{\partial}{\partial x} (Dv). \quad (29)$$

On rearranging, this gives

$$D = -\frac{1}{2v} \int_0^s (v \cdot s \cdot dx/t^{1/2}). \quad (30)$$

$$\text{Write } n = n_0 w, \quad \frac{dn}{ds} = v = n_0 \frac{dw}{ds} = n_0 \frac{dw}{dx} \frac{dx}{ds}.$$

$$\text{Hence we find} \quad D = -\frac{1}{2} \frac{dx}{dw} \int_0^w s \cdot dw. \quad (31)$$

s is determined by experiment as a function of w .

This equation is the one more generally applied, since D is usually a function of the concentration n .

Experimental details.

A different technique is applied according to whether the solution is coloured or uncoloured. In each case the containing vessel is small in size, $1.5 \times 0.5 \times 0.1$ cm., and diffusion takes place quickly. The choice of these small dimensions procures for Fürth and Zuber's method the great advantage of shortness of time needed to make a measurement. The time needed is of the order of a few minutes or, at most, an hour, and is very short compared with the period of the order of a week in earlier methods.

(a) Coloured liquids.

In this case two similar rectangular chambers with transparent glass walls are placed side by side (see fig. 1). One of them, called the diffusion chamber,

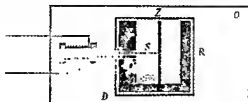


Fig. 1

has initially its lower half occupied by a solution of known concentration n_0 and the upper half is occupied by pure solvent, with a horizontal slider S separating the two halves. The other, called the comparison chamber, starts and remains full of a solution of a definite concentration n . At time $t = 0$ the slider S is removed from the first chamber and diffusion proceeds according to the theory previously discussed.

The chambers are fixed to the stage of an ordinary microscope of low magnification, with its tube in a horizontal position, and illuminated by a suitable source of light. A narrow horizontal slit can be moved up and down by means of a micrometer screw in the focal plane of the eyepiece. The position of the slit is adjusted from time to time, so that to the observer the two parts in front of the diffusion and comparison chambers appear equally bright, from which it follows that the concentration of the solute in the corresponding zone of the diffusion column has the value n . The height x of this zone above the slider level $x = 0$ is measured in this way. At a later time the height at which the concentration is n in the two chambers has a new value. Sets of values of x and t for this particular concentration are measured. Each set is used to plot a graph in which the ordinate is x and the abscissa is $t^{1/2}$. Each graph turns out to be a straight line passing through the origin (see fig. 4). Hence $x/t^{1/2} = s$ is a constant for a given concentration n . From a number of such graphs, sets of corresponding values of s and n are obtained, or, if we write $n/n_0 = w$, we get sets of corresponding values of s and w . Either graphically or algebraically we can express s as a function of w and also we can get ds/dw . Then in the general case, when D is not constant when n varies, D can be obtained from equation (31), namely

$$D = -\frac{1}{2} \frac{ds}{dw} \int_0^w s \cdot dw.$$

When the solution is very dilute, and if D is constant when n varies, D is calculated from equation (27), i.e.

$$D = x^2/4t\eta^2.$$

(b) *Colourless liquids.*

The method assumes that the refractive index of a solution for monochromatic light is a unique function of the concentration. A thin rectangular diffusion chamber is cemented to a wide face of a rectangular glass prism (see fig. 2). A parallel horizontal beam of monochromatic light falls on the hypotenuse face of the prism and after two refractions enters the diffusion chamber, which is at first filled with a liquid of uniform concentration n_1 . On looking at the ground-glass end wall of the diffusion chamber through a low-power micro-

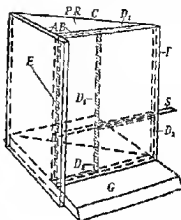
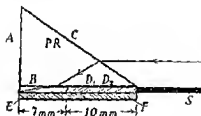


Fig. 2

scope, one can easily find a position of the latter when the left half of the image of the rectangular end face is dark and the right half bright, the line of separation, corresponding to the critical angle, being vertical. On rotating the prism anticlockwise

about a vertical axis through the middle point E of the ground-glass end, the vertical line of separation appears to move towards the right, eventually coinciding with the right-hand vertical wall as the whole image of the end becomes dark. (Note that the microscope gives a reversed image.) The prism is then clamped in position. The diffusion chamber while in the fixed position is next emptied, solution of a definite concentration is placed in the lower half, the slider inserted, and the upper half filled with pure solvent. At time $t = 0$ the slider is removed and upward diffusion commences. The concentration n is a function of x , the height above the central horizontal plane. The refractive index is also a

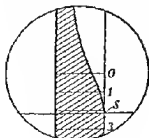


Fig. 3

slider level is the x of our theory, at which the concentration is π_1 , that of the first part of the experiment. As t changes the point S moves. A set of measured values of x and t tells us how a point of constant concentration π moves. It is found that x^2/t is a constant. The diffusivity is again calculated from

$$D = -\frac{1}{2} \frac{ds}{dw} \int_0^w s dw$$

when D is dependent on concentration, or

$$D = x^2/4t^2$$

when D is independent of concentration. The experiment (b) is repeated, beginning with a new concentration, and D is calculated as before.

F  rth calls an instrument designed to carry out the above two methods, a *microdiffusionmeter*. It resembles a spectrometer in having a rotating table to carry the diffusion chamber and prism, and a collimator to produce parallel light, but the telescope of the spectrometer is replaced by a microscope giving a magnification of about 20 diameters. The eyepiece of this microscope contains a horizontal "line" which can be adjusted vertically and its displacement measured by a micrometer screw. This serves to measure x in method (b). In method (a) the horizontal "line" is replaced by a fairly narrow horizontal slit. The source of light is a mercury arc provided with a filter transmitting only the green line $\lambda = 5461 \text{ \AA}$. Fig. 4 shows graphs representing a set of results for a coloured solution of a dye called congorubin in water. The first graph shows x plotted against $t^{1/2}$, and the second $D \times 10^6$ plotted against concentration. In this case D varies when the concentration varies.

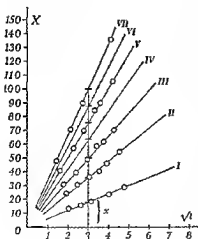
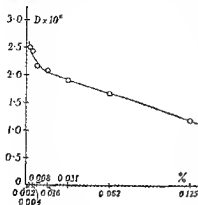


Fig. 4

By permission of Dr. F  rth and the "Journal of Scientific Instruments"

3. Osmotic Pressure and Diffusion.

Case I. *Solution with undissociated solute only.*

The osmotic pressure and the diffusivity of a solute in solution are connected in the following way. When the concentration of solute at one point *A* is greater than that at another point *B*, the osmotic pressure is also greater, by van't Hoff's law. The osmotic pressure may be regarded as a force giving the dissolved molecules an acceleration from one point to another point where the concentration is less. Consider the forces due to osmotic pressure, in the direction of increasing *x*, on an elementary cylinder of solution of unit cross-section (fig. 5). At *A* the force is *P* dynes, where *P* is the osmotic pressure. At *B* it is $- \{P + (dP/dx)dx\}$ dynes, and the net result is $(-dP/dx)dx$ dynes. If *n* is the concentration of molecules in this cylinder, the total number is *ndx*, for the volume is *dx* c.c. Hence it appears that *ndx* molecules experience an accelerating and diffusing force to the right, of value $(-dP/dx)dx$ dynes, so that the force per molecule is

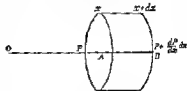


Fig. 5

$$-\frac{1}{n} \frac{dP}{dx} \text{ dynes} \quad (32)$$

Suppose that the motion of the molecules is impeded by retarding forces, such as the viscosity of the solvent, so that they acquire a constant terminal velocity, and that F_1 is the retarding force on each molecule when it is moving with a constant velocity of 1 cm. per sec. F_1 is also the driving force necessary to produce a terminal velocity of 1 cm. per sec. Hence a force of $(-1/n)(dP/dx)$ dynes produces a terminal velocity of $(-1/F_1)n(dx/dx)$ cm. per sec. The number of molecules crossing unit area near *A* per second is the number enclosed by a cylinder of length equal to the velocity and of cross-section 1 sq. cm. It is therefore

$$-\frac{1}{F_1} \frac{dP}{dx} \text{ molecules per sec.} \quad (33)$$

Now by van't Hoff's law $P = nk\theta$, where *k* is Boltzmann's constant, and this law holds for such solutions. Hence the number of molecules transferred across unit area per second is $(-k\theta/F_1)(dn/dx)$, and their mass is $(-mk\theta/F_1)(dn/dx)$ gm., where *m* is the mass of a molecule. This mass is also given by Fick's law of diffusion. In the statement of

that law on p. 258, the mass per c.c. is represented by n . Here we shall denote it by n_1 to avoid confusion, for we have used n for the number of molecules per c.c. Fick's law becomes $Q = -D \Delta dn_1/dx$. Also $n_1 = nm$ and $Q = -Dm \Delta dn/dx$. The mass transferred per unit area per second is $-Dm \Delta dn/dx$. On equating the two values of this mass just obtained we find that

$$K = \frac{k\theta}{F_1} \quad (34)$$

Case II. *Solution with one electrolyte, dissociated into two monovalent ions.*

Let the velocities of the cation (+) and anion (—) in a unit electric field, that is, the mobilities of the ions, be U and V cm. per sec. respectively. Each ion is driven along by the osmotic pressure like a molecule in case I above. As in that case, the force per cation is $(-1/n)(dP/dx)$ dynes, where n is now the concentration per c.c. of each kind of ion, and P is the total osmotic pressure of the solution. Again the velocity of a cation due to the osmotic pressure is $(-1/F_1 n)(dP/dx)$, that is,

$$-\frac{U}{n} \frac{dP}{dx} \quad (35)$$

and that of an anion is

$$-\frac{V}{n} \frac{dP}{dx} \quad (36)$$

As a rule $U \neq V$, so that if the osmotic pressure were alone responsible for the driving forces on the ions, the two kinds of ions would become separated. Another force, however, is called into play. For example, if an aqueous solution of HCl were placed at the bottom of a column of water, the hydrogen ions, the cations, would have a mobility U exceeding the mobility V of the chlorine anions. The liquid in such a vessel as is shown in fig. 6 would become positively charged near the top and negatively charged near the bottom, owing to the more rapid movement of the hydrogen ions towards the top. An electric field would thus be set up, which would reduce the velocity of the faster ions and increase that of the slower ions. A final state would be reached when the two kinds of ions travelled at equal rates, without separation.

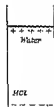


Fig. 6

Assuming this to occur, we may calculate the coefficient of diffusion. Let the electric field at any point in the solution, in the Ox direction, be X e.s.u., $= -dE/dx$ e.s.u., where E is the potential at that point. A monovalent ion at such a point experiences a force $\pm edE/dx$ dynes, according to the sign of its charge. Since the velocity of a cation

under unit force is U cm. per sec., a force $-e dE/dx$ produces a terminal velocity of $-UedE/dx$ cm. per sec. Similarly, the terminal velocity of an anion is $+VedE/dx$ cm. per sec. The total velocity of a cation due to both osmotic pressure and electric field is $-U(1/n \cdot dP/dx + edE/dx)$ cm. per sec., and of an anion $-V(1/n \cdot dP/dx - edE/dx)$ cm. per sec. We may assume from both experimental and theoretical considerations that the number of ions of each kind crossing unit area per second is the same, dN/dt , say. This quantity is also equal to the velocity of the ions concerned multiplied by their concentration, for it is the number of ions inside a cylinder of unit cross-section and length equal to the velocity. Hence

$$\frac{dN}{dt} = -U \left(\frac{dP}{dx} + ne \frac{dE}{dx} \right) = -V \left(\frac{dP}{dx} - ne \frac{dE}{dx} \right) \quad (37)$$

Eliminate dE/dx . This gives

$$\frac{dN}{dt} = - \frac{2UV}{(U+V)} \frac{dP}{dx} \quad (38)$$

According to van't Hoff's law, if all the n molecules per c.c. were ionized, each giving one ion of each kind, there would be altogether $2n$ ions per c.c. and the osmotic pressure would be $P_0 = 2n\lambda\theta$. But as has been mentioned above on p. 247, the actual osmotic pressure is $P = \beta P_0$, where β is a factor less than unity for dilute solutions. Then

$$\frac{dP}{dx} = 2\beta\lambda\theta \frac{dn}{dx} \quad (39)$$

and from equation (38)

$$\frac{dN}{dt} = - \frac{4\beta\lambda\theta UV}{(U+V)} \frac{dn}{dx} \quad (40)$$

Let the mass of each cation and anion be m_1 and m_2 gm. respectively. Then the total mass crossing unit area per second in one direction is

$$\begin{aligned} & - \frac{4\beta\lambda\theta UV(m_1 + m_2)}{(U+V)} \frac{dn}{dx} \\ & = - \frac{4\beta\lambda\theta UVm}{(U+V)} \frac{dn}{dx} \text{ gm. per sec.,} \end{aligned} \quad (41)$$

where m is the mass of one molecule of the solute. As in case 1, Fick's law gives the mass crossing unit area per second as $-Ddn_1/dx = -Dm dn/dx$, since $n_1 = nm$. By comparing the two equal masses we find that

$$D = \frac{4\beta\lambda\theta UV}{(U+V)} \quad (42)$$

4. Interdiffusion of Solids.

Though many solids have a definite crystalline structure, that is, a definite space lattice, it is found that two solids placed in contact diffuse into one another. Further, a solid metal *A* diffuses into a different solid metal *B* much more readily than it does into a second portion of *A* itself. Fick's law, $Q = -DA \, du/dx$, applies to solids, and the value of the diffusivity *K* has been obtained in certain cases.

Roberts-Austen investigated the diffusion of solid gold and other metals into lead. The lead was in the form of a cylinder 7 cm. long and 1.4 cm. in diameter. In one case a thin plate of gold was fused on one end of it in such a manner that immediately after the fusion the gold did not penetrate more than a millimetre into the lead. Then the cylinder was kept for about a month in a constant-temperature enclosure, at a temperature below the eutectic point of lead-gold alloys, that is, below their lowest melting-point. After this the cylinder was cut up into slices of equal thickness, and the quantity of gold in each was determined by chemical analysis. The balance used weighed to 2×10^{-5} gm. From the masses of gold in the slices, *K* was calculated by a method which is too long to reproduce here. In experiments by Seith and others, the apparatus was similar to that of Roberts-Austen, but the concentration of the diffusing metal in the slices was measured by the method of quantitative spectral analysis.

Groh and Hevesy early used a novel method (now familiar as the modern radioactive-tracer technique) in their determination of the coefficient of diffusion of solid lead in solid lead, that is, the self-diffusivity of lead. To a rod of ordinary pure lead, 1.5 cm. long, was fused a rod, 0.5 cm. long, of Joachimsthal lead, which is a mixture of three isotopes, namely, ordinary lead, uranium lead, and radium D. Of these, radium D alone is radioactive. The electron shells of all three isotopes, and therefore the "sizes" of the atoms, were assumed to be the same. In effect, the conditions as regards diffusion were the same as if ordinary lead were diffusing into ordinary lead. The time allowed for diffusion was about 400 days. Then the rod which was originally ordinary lead was cut into slices, and the α -ray activity of each slice was measured by means of an α -ray electroscope. These α -rays came from the polonium formed by radioactive disintegration of the radium D which had diffused, and hence the mass of the latter in each slice could be calculated. It was assumed that the proportions of the three isotopes diffusing were the same as in Joachimsthal lead; the total mass of diffused lead in each slice was calculated, and hence the diffusivity.

While diffusion in gases can often be approximately treated simply in terms of concentration gradient and kinetic theory, it is not surprising that in the condensed state the interatomic forces play a dominant role. Diffusion in a perfect solid occurs by the following mechanism. Owing to statistical fluctuations in the vibrational kinetic energy associated with any particular atom, certain atoms will occasionally receive energy greater than the interatomic binding energy which keeps the atom at its normal lattice point. At the surface of the solid this gives rise to evaporation, but in the interior it results in the atom being temporarily ejected into the space between two normal lattice points. This creation of an interstitial atom is accompanied by the creation of a vacant site from which the atom has been ejected. This vacant site

may now be refilled by the interstitial atom returning to its original position, but it may alternatively be filled by a second atom moving from adjacent lattice points into the first vacancy. In so doing, the second atom creates a vacancy at the position from which it has come. A wandering of the vacant sites is thereby set up which constitutes a diffusion of vacancies, and a complementary diffusion of interstitial atoms may occur as they are forced by thermal agitation from one interstitial position to another. The diffusion rate will clearly be accelerated if crystalline imperfections occur such as exist in real crystals. Dislocation lines and planes where the atoms are displaced relatively to each other are normally present in most real solids, and these defects may be accompanied by increasingly grosser defects, such as actual vacant single sites, aggregate vacant sites and eventually microscopic cracks.

No simple approximate relation between diffusion constant and temperature such as $D \propto T^3$, which applies to gases, can be expected for solids, but diffusion rate will clearly increase with temperature, the general expression being of the form $D = D_0 \exp(-E/kT)$ where E is the so-called *activation energy*, that is, the energy barrier which has to be surmounted for an atom to move from one position to an adjacent

would be expected to depend on the magnitude of the ratio E/kT as found. In some crystals the diffusion process may be assisted by an inert tracer atom, which is not a self-interstitial atom, but which is a stable atom. In such cases the tracer atoms will not take place at quite the same rate as for stable atoms, because the lack of exact equivalence of the tracer atom and its inert neighbours will lead to a greater tendency of the freshly created interstitial tracer atom to return to the immediate vacant site from which it has just come. This behaviour would lead to lower values of D when measured by the radioactive-tracer technique and this is confirmed experimentally.

CHAPTER XII

Viscosity

1. Newton's Law of Viscous Flow.

When a liquid flows over a fixed surface such as AB (fig. 1), it is found experimentally that a layer D at a distance $x + dx$ from AB flows with a velocity greater than that of a layer at C , a distance x from AB . If the difference in the velocities of the two layers is dv , the velocity gradient between C and D will be dv/dx . As a result of this relative motion of the layers, *internal friction* or *viscosity* arises. Newton's law of viscous flow for streamline motion (as opposed to turbulent flow) is

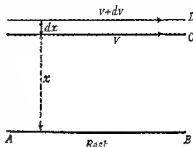


Fig. 1

$$F = \eta A \frac{dv}{dx} \quad \dots \dots \dots (1)$$

where F is the tangential viscous force between two layers of area A a distance dx apart, moving with relative velocity dv . The quantity η is termed the *dynamical coefficient of viscosity* of the liquid.

2. Fugitive Elasticity.

There are two theoretical modes of approach to problems involving viscosity. The first is by analogy with the elastic properties of solids, and the second by consideration of the implications of the kinetic theory of matter. The former mode of approach is more applicable to the discussion of the viscosity of liquids and the latter to the viscosity of gases.

Maxwell considered that a liquid possesses a certain amount of rigidity but is continually breaking down under the shearing stress.

The analogy is emphasized by the formal similarity between the two equations

$$\text{Rigidity } n = \frac{\text{stress}}{\text{strain (shear)}} = \frac{P}{\theta} = \frac{P}{dy/dx} \quad (2)$$

$$\text{Viscosity } \eta = \frac{\text{stress}}{\text{velocity gradient}} = \frac{P}{dv/dx} \quad (3)$$

A liquid is therefore regarded as exerting and sustaining a certain amount of shearing stress for a short time, after which it breaks down and the shear is reformed. Let the rate at which the shear breaks down be proportional to its value θ , and be given by $\lambda\theta$. If y is the displacement, $\theta = dy/dx$, and the rate of formation of shear $= d\theta/dt = \frac{d}{dt} \left(\frac{dy}{dx} \right) = \frac{d}{dx} \left(\frac{dy}{dt} \right) = \frac{dv}{dx}$. Thus

$$\lambda\theta = dv/dx \quad (4)$$

when the steady state of flow of liquid has been reached. Hence from (2), (3) and (4),

$$\eta = n/\lambda \quad (5)$$

The quantity $1/\lambda$ is termed the *time of relaxation* of the medium and measures the time taken for the shear to disappear when no fresh shear is applied.

Pursuing the analogy between elasticity and viscosity, it may be noted that in addition to the shear viscosity a *dilatational viscosity* may occur. This arises when a volume of liquid is compressed or dilated without change of shape. So far little investigation has been made of this subject, but the introduction of dilatational viscosity into acoustical calculations eliminates an apparent discrepancy which exists between theory and observation on the absorption of sound in liquids at high frequency.

3. Methods of Determining η .

All the methods used for determining η require the flow to be streamline. The necessary and sufficient conditions for this criterion to be fulfilled will be considered later (p. 275).

The main methods available for determining the coefficient of viscosity of liquids fall into two groups, the first involving the measurement of the rate of flow of a liquid through a capillary tube, and the second involving observation of the motion of a solid body moving through the liquid.

4. Flow Methods: Poiseuille's Formula.

The following formula for the volume of liquid flowing per second

through a cylindrical tube of circular cross-section is due to Poiseuille. Its validity rests on three conditions:

- (1) there must be streamline flow;
- (2) the pressure must be constant over any cross-section, that is, no radial flow must occur;
- (3) the liquid in contact with the walls of the tube must be at rest.

We assume that these conditions are satisfied and that a steady flow of liquid is in progress. Let the velocity of the liquid (fig. 2) at a distance r from the axis be v ; then the velocity gradient will be dv/dr and the tangential stress $\eta dv/dr$. If a pressure difference p exists between two points in the tube a distance l apart, the force causing motion of the volume of the cylinder of liquid of radius r is πpr^2 .

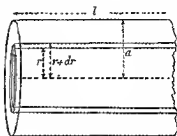


Fig. 2

Hence, equating this accelerating force to the retarding viscous force, we obtain the condition for steady flow, namely

$$p\pi r^2 = -\eta \frac{dv}{dr} 2\pi r l$$

$$\text{or} \quad \frac{dv}{dr} = -r \frac{p}{2\eta l} \quad \dots \dots \dots (6)$$

The velocity gradient is therefore proportional to r , the distance from the axis of the tube, and vanishes on the axis.

At the wall of the tube $r = a$ and $v = 0$: integrating from $r = a$ to $r = r$, we have

$$a^2 - r^2 = \frac{4\eta l v}{p}$$

$$\text{or} \quad v = \frac{p}{4\eta l} (a^2 - r^2). \quad \dots \dots \dots (7)$$

The profile of the advancing liquid is therefore a parabola.

The volume of liquid dQ flowing through the tube per second between the radii r and $r + dr$ is given by

$$dQ = 2\pi r v dr.$$

Hence the total volume of liquid flowing through the tube per second is

$$Q = \int_0^a \frac{p\pi}{2\eta l} (a^2 - r^2) r dr = \frac{\pi p a^4}{8\eta l} \quad \dots \dots \dots (8)$$

An accurate and convenient method for determining η by Poiseuille's method

tubing about 5 mm. in diameter and these are slipped over the narrower tube. The centres of the T-tubes are adjusted so as to lie over the fine holes in the central

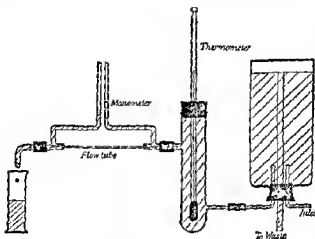


Fig. 3

tube, and the joints between the two tubes are then sealed with wax so as to render the system watertight. The T-tubes are connected to two upright glass tubes forming a manometer, and the pressure difference over the distance l is thus measured directly. The remainder of the apparatus is shown in the diagram, the part on the right being a device to maintain a constant head of water.

5. Corrections to Poiseuille's Formula.

With the apparatus described above Poiseuille's formula requires no corrections if the flow of liquid is slow,* the experimental conditions approaching the ideal as the pressure-holes are diminished in size. In many experimental arrangements, however, the excess pressure is often regarded as that due simply to the head of water at the inlet end. Two sources of error must then be considered:

- (1) Accelerations occur near the inlet to the tube, the velocity distribution

* If the flow is fast, a correction for the kinetic energy imparted to the liquid must be made, as is explained in (2) below.

being non-uniform until a short length of the tube has been traversed. To correct for this a quantity πa must be added to l , where $\pi = 1.64$ approximately.

(2) The pressure difference between the two ends is used partly in communicating kinetic energy to the liquid and not wholly in overcoming viscous resistance.

An approximate value of the correction for the latter may be obtained in the following way. The kinetic energy given to the liquid, of density ρ , per second is

$$\begin{aligned} \frac{1}{2} \rho \int_0^a 2\pi r v^2 dr &= \pi \rho \left(\frac{p}{4\eta l} \right)^2 \int_0^a r(a^2 - r^2)^2 dr \\ &= \pi \rho \left(\frac{p}{4\eta l} \right)^2 \frac{a^5}{8} = \left(\frac{\pi \rho a^4}{8\eta l} \right)^2 \frac{p}{\pi^2 a^4} \quad \dots (9) \end{aligned}$$

The work done in overcoming the viscosity is pQ ; the total loss of energy per second is therefore

$$pQ + \frac{Q^2 \rho}{\pi^2 a^4} \quad \dots (10)$$

If the total external pressure is p_1 , then

$$p_1 Q = pQ + \frac{Q^2 \rho}{\pi^2 a^4}$$

or

$$p = p_1 - \frac{Q^2 \rho}{\pi^2 a^4} \quad \dots (11)$$

This correction has been tested experimentally by Hagenbach, by Couette and by Wilberforce, but it is only approximately true, and according to some authorities (Edser), the correction is twice that given by (9). In the form given here it implies a radial pressure gradient at the end cross-section of the tube. The correction should be $-mQ^2\rho/\pi^2 a^4$, where m is found experimentally to be approximately unity; its value must be obtained by calibration, if accurate results are required.

The complete corrected formula is therefore

$$\eta = \frac{\pi p_1 a^4}{8Q(l + 1.64a)} - \frac{mQ\rho}{8\pi(l + 1.64a)} \quad \dots (12)$$

6. Critical Velocity.

Poiseuille's formula is valid only so long as the flow of liquid in the tube is streamline. This condition is fulfilled at low velocities and for tubes of small radius. It is convenient to remember that for a tube 50 cm. long, of bore about 3 mm., the pressure difference between the ends of the tube must not be greater than about 3 cm. when water is used. The velocity (V_c) at which turbulent flow sets in is termed the *critical velocity*. It can be shown by the method of dimensional analysis that $V_c = k\eta/\rho a$, where η is the coefficient of viscosity of the liquid, ρ its density, and a the radius of the tube. The ratio η/ρ is frequently denoted by ν and termed the *kinematic viscosity*. The quantity k is termed *Reynolds' number* and generally has a value about 1000. The relation between the volume of liquid Q and the pressure p is shown in fig. 4.

At low velocities, that is, when the motion is streamline, Q is proportional to p , in agreement with Poiseuille's relation. As the rate of flow is increased beyond the critical velocity, however, the quantity

flowing through increases less rapidly and soon becomes independent of the viscosity of the liquid and dependent mainly on the density. Com-

quite turbulent, the quantity flowing is nearly proportional to the square root of the pressure. The pressure difference is now used up in overcoming the turbulent motion and communicating kinetic energy to the liquid. The fact that the rate of turbulent flow is independent of the viscosity explains the rapid flow of viscous lava from volcanoes. The effect may be demonstrated in the laboratory by introducing a small quantity of coloured liquid along the axis of a tube. While stream-

line flow is in progress, the coloured liquid is drawn out into a thin filament parallel to the length of the tube. As soon as turbulent flow sets in, the filament becomes wavy and spreads out, the coloured liquid eventually filling the entire tube.

It may be shown, by a simple extension of the theory leading to Poiseuille's formula, that the presence of an axial wire, of diameter only $1/1000$ that of the tube, should reduce the flow by about 15 per cent. Lea and Tadros experimentally found that the reduction was much less than this, except

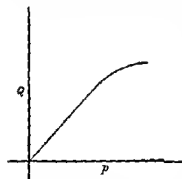


Fig. 4

when the radius of the core approached one-half the radius of the tube; then theory and experiment were in good agreement. With a core present, the critical velocities are much lower, and local turbulence at the boundary of the core co-existing with streamline flow in the bulk of the liquid in the tube is found to account adequately for the discrepancy.

7. Accurate Determination of η .

To avoid the use of the uncertain Hagenbach correction, the standard viscometer is made in a form suggested by Couette: the following arrangement is used at the *Reichsanstalt* (fig. 5).

The liquid flows from the reservoir *A* through the two capillaries K_1 , K_2 which are connected in series, to the outlet *P*, where the volume is measured *V*.

two capillaries are given directly by the heights h_1 , h_2 and h , of the liquid in the

tubes M_1 , M_2 and M_3 . The heights are determined with a cathetometer. Since the correction is the same for both tubes, we have

$$\eta = \frac{\pi}{8Q} \frac{a_1^4(p_1 - p_2) - a_2^4(p_2 - p_3)}{l_1 - l_2}.$$

The expression takes a much simpler form if $a_1 = a_2$, but this is difficult to realize experimentally.

Viscometers which are simple to use but which require calibration are available commercially in a variety of forms. The type invented by Ostwald is described here (fig. 6).

The liquid, which is initially introduced through A into the bulb B , is sucked into the bulb C through the capillary K until a mark m_1 is reached. The time t taken for the meniscus to fall vertically under gravity from m_1 to m_2 is then observed. Since with such an arrangement the effective pressure difference is proportional to the density ρ

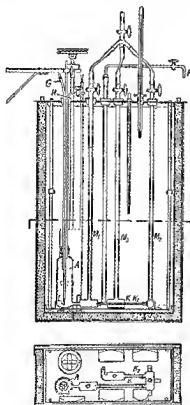


Fig. 5*

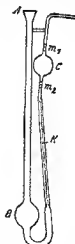


Fig. 6

of the liquid, the Poiseuille formula, together with the Hagenbach correction, may be written

$$\eta = A\rho t - \frac{B\rho}{t}, \quad \dots \dots \dots (13)$$

* This figure, together with figs. 6, 8, 9, 11, 12, 13, 14 of this chapter, are taken from Wien-Harms, *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig).

where A and B are constants which must be determined with two liquids of known viscosity. The instruments are generally so constructed that the correction term may be neglected; a single calibration is then sufficient.

To determine the viscosity of molten metals, an instrument of the Ostwald type is generally used, the flow tube being constructed of quartz or silver. The passage of the meniscus past two fixed points is recorded electrically. For non-

volume change.

8. Other Methods for Measuring η .

The second general method of measuring viscosity, in which a body moves in a liquid, has many variations, which may be classified as follows.

- (1) The rotation viscometer.
 - (2) Maxwell's oscillating disc.
 - (3) Stokes's method, by the damping of a pendulum vibrating in the liquid.
 - (4) Damping of a solid sphere vibrating about a diameter and immersed in the liquid.
 - (5) Damping of the vibrations of a hollow sphere filled with the liquid.
 - (6) Stokes's falling-body viscometer.
- Methods (1) and (6) will be considered here in detail.

9. The Rotation Viscometer.

Consider two concentric cylinders of radii a , b , the space between them being filled with the liquid whose viscosity is required (fig. 7).

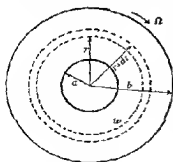


Fig. 7

If the outer cylinder is rotated with uniform velocity, a torque is communicated to the inner cylinder, the magnitude of which may be registered by suspending it from a torsion wire. We consider the motion of any concentric cylinder of liquid of radius r , let its angular velocity of rotation be ω . Then the velocity gradient at this point will be

$$\frac{d}{dr}(r\omega) = \omega + r \frac{d\omega}{dr}. \quad (14)$$

The first term on the right-hand side represents the angular motion which the layer would have if no viscous slip occurred; the second term is responsible for the viscous stress introduced, and if we apply

Newton's law, the viscous torque Γ over unit length of the surface of the cylinder will be

$$\Gamma = 2\pi\eta r^3 \frac{d\omega}{dr}. \quad . \quad . \quad . \quad (15)$$

When the steady state is reached, this torque must be equal to that exerted on the inner cylinder. Hence, integrating equation (15) and using the conditions $r = a$, $\omega = 0$, and $r = b$, $\omega = \Omega$, where Ω is the angular velocity of the outer cylinder, we have

$$\Gamma = 4\pi\eta\Omega \frac{a^2b^2}{(b^2 - a^2)}. \quad . \quad . \quad . \quad (16)$$

The torque over the base of the inner cylinder has been neglected in this treatment; in practice the correction is eliminated by measurements with two different lengths of cylinder immersed. Representing the torque on the base by $f(B)$, we have, for depths of immersion l_1 and l_2 ,

$$\Gamma_1 = 4\pi\eta\Omega \frac{a^2b^2}{(b^2 - a^2)} l_1 + f(B),$$

$$\Gamma_2 = 4\pi\eta\Omega \frac{a^2b^2}{(b^2 - a^2)} l_2 + f(B).$$

Hence

$$\Gamma_1 - \Gamma_2 = 4\pi\eta\Omega \frac{a^2b^2}{(b^2 - a^2)} (l_1 - l_2). \quad . \quad . \quad (17)$$

The torque may be measured in two ways: (i) by the twist produced in a suspension of known rigidity; (ii) by using a fixed external cylinder and measuring the angular velocity of rotation of the internal cylinder when a known couple is applied.

As typical of the first method, we shall consider *Hatchell's viscometer* (fig. 8).

A wooden cylinder A is suspended by a torsion wire B from a fixed support C . The outer coaxial cylinder D is rotated by the pulley G , which is coupled to an electric motor. The space E may be used to provide an electrically heated water-bath. The cylinders F and F' are introduced to act as guard rings, and end corrections for the cylinder A are thus avoided.

In *Searle's method*, a diagram of which is given in fig. 9, the inner cylinder a is pivoted about a vertical axis b and rotates under the couple provided by the weights in the scale-pans c . The couple is transferred by cords passing over frictionless pulleys d to a drum e . The outer cylinder f can be raised or lowered by rotating the ring g . The speed of rotation is determined with a stop-watch, by observing the transits of the point i over the circular scale h . The apparatus is stopped or released by raising or lowering the stop k .

As in the case of Poiseuille's formula, the validity of application of the theoretical formulae to the experiments with the rotation viscometer depend on the condition of streamline flow. The relation

between Ω and Γ is shown in fig. 10. When Ω is small the motion is streamline and Γ is proportional to Ω ; when turbulent motion first sets in the relation becomes irregular. At higher speeds Γ becomes approximately proportional to Ω^2 . The relations are therefore exactly similar to those which exist between the quantity of liquid flowing

per second through a right circular cylinder and the pressure difference between the ends.

Taylor* has investigated the transition from streamline to turbulent motion for concentric cylinders. Above the critical velocity, the liquid contains helical vortices situated at regular intervals parallel to the axis of rotation and at a distance apart approximately equal to $(b-a)$, measured in the same direction.

Reynold's method for investigating turbulent motion has been improved by Andrade and Lewis,† who substitute colloidal particles for the usual colouring matter. The method has two advantages (i) the velocity distribution may be found by illuminating and photographing with a known exposure, since each particle traverses a distance proportional to its velocity, (ii) since

interdiffusion does not occur, the phenomena may be observed for any length of time.

10. Stokes's Falling-body Viscometer.

From hydrodynamical considerations of a perfectly homogeneous continuous fluid of infinite extent, Stokes derived the relation $F = 6\pi\eta av$ for the viscous retarding force F on a moving with uniform velocity v a sphere of radius a in a fluid of viscosity η . For a sphere falling

$$6\pi\eta av = \frac{4}{3}\pi a^3(\rho - \sigma)g, \quad (18)$$

where ρ is the density of the sphere and σ that of the liquid. Since the

* Taylor, *Phil. Trans. A*, Vol. 223, p. 387 (1927).

† Andrade and Lewis, *Journ. Sci. Inst.* Vol. 1, p. 373 (1924).

terminal velocity v may be measured from the time of transit between two fixed marks on the sides of a vertical glass tube, this furnishes a convenient method for finding η .

If the total height of the liquid contained in the tube is divided into three equal parts, the centre division being used for the velocity determination, Ladenburg has shown that in order to correct for the finite extent of the liquid, the equation should be

$$\eta = \frac{2}{9} \frac{(\rho - \sigma)ga^2}{v} \frac{1}{(1 + 2.4a/R)(1 + 3.3a/h)} \quad (19)$$

where R is the radius of the tube and h the total height of the liquid.

Faxén has given a still more accurate correction; if η_s is the co-

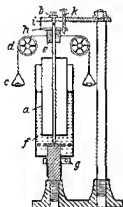


Fig. 9

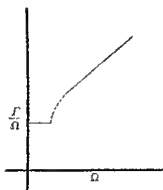


Fig. 10

efficient of viscosity as calculated from the uncorrected Stokes's law, then the true viscosity is given by $\eta = \eta_s \{1 - 2.104(a/R) + 2.09(a/R)^2 - 0.95(a/R)^3\}$. With spheres, therefore, the simple Stokes's law gives a value of η correct to one per cent if $R/a > 200$. Any departure from sphericity requires far greater correction; for example, cylinders falling in glycerine give an apparent viscosity twice the accepted value owing to the boundary effect, even for $R/a > 500$. Consideration of the deviations from Stokes's law which occur during the fall of small drops through gases is of great importance, since Millikan's experiment for the determination of the charge on the electron is based on this principle.

11. Viscosity of Gases.

All the methods considered for the determination of the viscosity of liquids are applicable to gases if certain modifications are made in the experimental technique and in the associated formulae.

(1) *Extension of Poiseuille's Method.*

As a liquid is assumed to be incompressible under the conditions of the experiment, the equation $Q = -(\pi a^4/8\eta) dp/dx$, which is a differential form of equation (8), p. 273, may be integrated directly. For a gas, however, the density will decrease along the tube, and we have now to express the fact that the mass and not simply the volume traversing any cross-section is constant.

If ρ represents the density and Q the volume passing any cross section per second, $\rho Q = \text{constant}$ or $pQ = \text{constant}$, since the density is proportional to the pressure. Then if p_1 is the pressure at the inlet of the tube and Q_1 is the volume entering per second,

$$p_1 Q_1 = pQ = -\frac{\pi a^4}{8\eta} \rho \frac{dp}{dx}; \quad (20)$$

or

$$\int_0^l p_1 Q_1 dx = -\frac{\pi a^4}{8\eta} \int_{p_1}^{p_2} p dp,$$

where p_2 is the pressure at the outlet. Hence

$$p_1 Q_1 = \frac{(p_1^2 - p_2^2)}{16\eta l} \pi a^4. \quad (21)$$

The complete formula, when the Hagenbach correction and also the slipping which occurs at the sides of the tube are taken into account, has been shown by Erk* to be

$$\eta = \frac{\pi a^4}{16l p_1 Q_1} (p_1^2 - p_2^2) \left(1 + \frac{4\delta}{a}\right) - \frac{p Q_1}{8\pi l} \left(m + \log_e \frac{p_1}{p_2}\right), \quad (22)$$

* Erk, *Zeits. f. techn. Phys.*, Vol. 10, p. 452 (1929)

(2) *Rankine's Method.*

There are many experimental methods for determining the viscosity of a gas by means of a pellet of mercury which slides down a vertical tube and forces the gas through a capillary tube during the descent. A convenient arrangement due to Rankine is shown in fig. 12.

A capillary tube K and a wider tube D are joined as shown to form a closed system. A drop of mercury E slides between two fixed marks A and B in the wide tube and thus traverses a volume Q , which is equal to the volume of gas which flows through the capillary tube. The general equation connecting t , the time of fall of the drop, and m , its mass, is

$$t = \frac{\beta}{(m - \alpha)} \quad (23)$$

* Erk, *Zeits. f. techn. Phys.*, Vol. 10, p. 452 (1929)

where α and β are constants, the former depending on the surface tension and being commonly known as the *sticking coefficient*. It may be eliminated by performing experiments with pellets of two different masses. The effective pressure difference is given by $p = \beta g / \Delta t$, where A is the area of cross-section of the fall-tube. Hence if we neglect the Hagenbach correction, formula (21) becomes approximately

$$\eta = \frac{m^2 \beta g}{8 \lambda Q t A} \left(1 + 4 \frac{L}{r} \right). \quad \dots \dots \dots (24)$$

Since β is constant, the apparatus is convenient for comparing the viscosities of different gases. Alternatively, steam or liquid at a known temperature may be

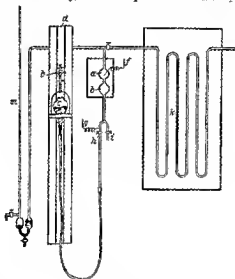


Fig. 11

circulated through PQ and the variation of viscosity with temperature may be investigated.

(3) *Edwards' Constant Volume Method.*

In contrast to the two methods previously described, in which the viscosity is measured at constant pressure, Edwards has devised a method, as shown in fig. 13, for determining η at constant volume.

Gas is contained in the large bulb B at a pressure p_1 which is registered by the mercury in the arms of the manometer ab . The tap T_1 is then closed and T_2 opened to atmosphere for a certain time t . Finally T_2 is closed and the new pressure p_2 is observed. Let the volume of the bulb be Q . Then if Q_1 is the volume of gas entering the capillary tube K per second at time t when the pressure in the apparatus is p , for a slow rate of flow

$$pQ = (p \div dp)(Q \div Q_1 dt).$$

when p changes to $p + dp$ in time dt . Hence

$$pQ_1 = -Q \frac{dp}{dt} \text{ approximately.}$$

But

$$pQ_1 = \frac{\pi a^4 (p^2 - p_0^2)}{16\eta l},$$

where p_0 is the atmospheric pressure. Hence

$$\frac{\pi a^4 t}{16\eta l Q} = - \int_{p_1+p_0}^{p_2+p_0} \frac{dp}{p^2 - p_0^2} = \frac{1}{2p_0} \log \frac{(p_1 + 2p_0) p_2}{(p_2 + 2p_0) p_1}.$$

If the slipping coefficient is also considered, we have

$$\eta = \frac{\pi a^4 t}{8lQ} \frac{p_0 \left(1 + 4 \frac{k}{r}\right)}{\log \frac{(p_1 + 2p_0) p_2}{(p_2 + 2p_0) p_1}} \quad \dots (25)$$

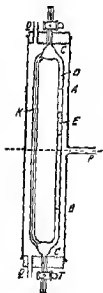


Fig. 12

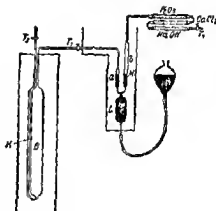


Fig. 13

(4) Maxwell's Oscillating-disc Viscometer.

The rotation viscometer of Hatschek (pp.279-80) may be applied directly to the determination of the viscosity of gases

As typical of the viscometers dependent on damping, Maxwell's oscillating disc will now be described; the rate of damping is approximately proportional to the viscosity of the gas. In instruments of this type the expansion of the gas which is inevitable in the flow methods is avoided, and it was with the oscillating disc that Maxwell's prediction from the kinetic theory, that the viscosity should be independent of the pressure, was verified. The viscosity of gases at very

low temperatures has been determined with a recent form of the apparatus due to Vogel* (fig. 14).

A thin glass disc dd was attached by a nickel wire to the mirror a , the whole being suspended by a fine platinum wire from the hook k . A rotation head c enabled the zero to be set easily. The fixed plates were clamped by the clamps FF to two fixed pieces MM . The gas was introduced through E and the apparatus was set in operation magnetically by means of the astatic pair of magnets ff . While the lower part of the apparatus could be immersed in any desired temperature bath, the platinum suspension was sufficiently distant for its elastic properties to remain constant.

The theory of the instrument is complicated and involves many uncertain corrections, so that the method is suitable only for comparison and not for absolute measurements. The corrections may be avoided to some extent by the use of a guard ring. The method has useful applications in the determination of the viscosity of molten metals, since the inertia of the liquid is large and the mass movements of the liquid are small, hence the size of the vessel is unimportant and the use of a guard ring becomes unnecessary. The flow methods lead to considerable error unless precautions are taken to avoid oxidation, and the apparent viscosity is often greatly increased by the formation of a skin of impurities on the surface of the flow tube.

12. Variation of the Viscosity of Fluids with Pressure.

(1) Liquids.

Little work was done on the variation of the coefficient of viscosity of liquids with pressure before Bridgman (p. 93).

In certain qualitative features the behaviour of all liquids, except water, is similar, although there are large quantitative differences. The viscosity of liquids increases with pressure at a rapidly increasing rate. Reference to Chapter V shows this to be unusual, most pressure effects diminishing as the pressure is increased. The behaviour of water is exceptional. Between 0° C. and 10° C. there is a minimum viscosity at about 1000 kg./cm.^2 . At 30° C. and 75° C. experiments showed that the minimum had disappeared, and a regular increase of viscosity with pressure was observed. No really satisfactory theory of the variation of the viscosity of liquids with pressure has yet been proposed.

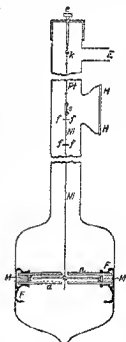


Fig. 14

* H. Vogel, *Ann. d. Physik*, Ser. 4, Vol. 43, p. 1236 (1914).

(2) *Gases.*

It is shown in Chap. IX (p. 197) that according to the kinetic theory of gases the coefficient of viscosity should be independent of the pressure at ordinary pressures. At low pressures, on the other hand, when the mean free path of a gas molecule becomes greater than the linear dimensions of the containing vessel, the kinetic theory shows (p. 201) that η should be proportional to p . Both predictions are in good agreement with experiment. At very high pressures, Bridgman has shown that the coefficient of viscosity of gases increases with increasing pressure. The problem has recently received independent investigation by Boyd, who has shown that the Hagenbach correction becomes increasingly important at higher pressures.

Highly purified nitrogen and hydrogen and mixtures of the two were passed through a steel flow tube at pressures up to nearly 200 atmospheres. The maximum relative increase in the viscosity of nitrogen was 25 per cent, of hydrogen 10 per cent, and of the mixture 20 per cent. Further work by Michels and Gibeon,

13. Variation of Viscosity of Fluids with Temperature.

(1) *Liquids.*

The viscosity of liquids decreases rapidly with rise of temperature. For water, the viscosity at 80° C. is only one-third of its value at 10° C. Although the relationship has been the subject of many investigations, no satisfactory simple formula has been suggested which expresses the connexion with any great degree of accuracy. The empirical formula of Slotte,

$$\eta = \frac{\eta_0}{1 + \alpha t + \beta t^2} \quad \dots \dots \dots (26)$$

where α and β are constants, is only in approximate agreement with experiment, while a modification

$$\eta = \frac{A}{(1 + Bt)^C} \quad \dots \dots \dots (27)$$

where A , B and C are constants, is cumbersome and does not apply to the important practical case of oils, which are mixtures of chemical compounds not easily separable. Owing to the lack of a satisfactory theory of liquids, no theoretical relation of any value was derived until the work of Andrade.*

On Andrade's theory, a liquid is considered to consist of molecules vibrating under the influence of local forces about equilibrium positions which, instead of being fixed as in a solid, are slowly displaced with

* Andrade, *Phil. Mag.*, Vol. 17, p. 698 (1934)

time. The liquid state is here regarded as being closer to the solid state than to the gaseous state. At extreme libration (compare Lindemann's theory of fusion *) a molecule of one layer may momentarily combine with one of an adjacent parallel layer, supposed to be moving past it with a drift velocity given by the bulk velocity gradient, the combination being of extremely short duration but sufficing to ensure a sharing of momentum parallel to the drift. If the frequency of vibration of a liquid at the melting-point is taken as that of the solid form at the same temperature, a coefficient of viscosity can be calculated for simple substances in the liquid state which agrees closely with the experimental value. Communication of momentum takes place only if the mutual potential energy, probably determined by the relative orientation of the approaching molecules, is favourable. Under the influence of local intermolecular forces the molecules tend to be similarly orientated within very small groups, the boundary and molecular population of each group changing continually. The tendency to orientation which is favourable for interchange of momentum is disturbed by the thermal agitation. On this basis the formula

$$m^{\dagger} = Ae^{cfoT} \quad (28)$$

is derived for the variation of viscosity with temperature, A and c being constants and v the specific volume. This formula agrees closely with experiment for all liquids so far examined, except water and certain tertiary alcohols. It applies to ordinary associated liquids as well as to non-associated liquids, although the meaning to be attributed to the constant c is somewhat different in the two cases.

More recently, theories of the liquid state based on the cell model and the hole model have given expressions similar to equation (28), indicating a diffusion coefficient proportional to $e^{-E/kT}$ and a viscosity coefficient proportional to $e^{E/kT}$, for the viscosity is by definition inversely proportional to the rate of fluid flow at any selected pressure gradient. In the cell model a typical molecule in the liquid is regarded as being confined to a cell surrounded by a potential barrier of height E . Under thermal agitation, the number of molecules which have energy greater than E is given by Boltzmann's theorem as $e^{-E/kT}$. We have already mentioned in Chapter XI, § 4, that diffusion in solids shows such a temperature variation.

In the hole model a liquid is regarded as a solid in which the whole lattice structure has broken down, so that molecules have migrated from various lattice points to form clusters of interstitial atoms and left behind vacant sites which have aggregated into holes. Flow of liquid then corresponds to transfer of molecules from interstitial clusters to holes, and the rate of transfer will depend on the number of available holes. Since the creation of a vacant site or hole requires some activation

* See Roberts, *Heat and Thermodynamics*, fourth edition, p. 551.

energy E against the surrounding intermolecular forces, a thermally controlled system will give a number of vacancies proportional to $e^{-E/RT}$.

(2) Gases.

The viscosity of all gases increases with rise of temperature. For a discussion of the results reference should be made to Chapter IX, p. 197.

14. Viscosity of Mixtures and Solutions; Variation with Chemical Constitution.

A large number of experiments have been made on the viscosity of mixtures and of solutions, but no general laws have resulted in either case. With some solutions the viscosity is less than that of the pure solvent, while with others it is greater, reaching a maximum for a certain concentration. With mixtures, the viscosity is generally less than the arithmetic mean of the viscosities of the components of the mixture. Again, the dependence on chemical constitution is anything but straightforward, experiments by Pendersen on the ethers show a very general decrease in viscosity with increasing molecular weight, although many exceptions occur.

15 Non-Newtonian Fluids.

Many commonly occurring fluids, for example colloids and pastes, are non-Newtonian in their viscous behaviour in that the rate of shear is not proportional to the shearing stress, or is proportional over only a very limited range of pressure. The volume discharged through a capillary tube is therefore not proportional to the pressure, and application of the formula derived hitherto will have meaning only when the conditions are specified. The science of fluid flow in general is termed *rheology*, and Newtonian fluids constitute a very limited section.

If a fluid shows an isothermal reversible decrease of viscosity with increase in the rate of shear it is termed *thixotropic*. The ideal lubricant is one which has a very high viscosity at almost zero shear when the machinery is at rest, so that once the lubricant has been drawn into the bearings against gravity by surface tension forces, it will stay there; then when the machinery gathers speed the lubricant exhibits its thixotropic property of decrease of viscosity with increasing rate of shear, so producing minimum friction and power loss.

To study further the behaviour of *thixotropic* substances we may consider equation (1) to be modified to $F = \eta_0 du/dx + \theta$, where η_0 is the Newtonian coefficient of viscosity and θ is the coefficient of thixotropy. We have seen that η_0 decreases rapidly with temperature; on the other hand, θ is almost independent of temperature. This behaviour throws some light on the nature of thixotropy, which receives explanation in terms of a structure of the fluid. The particles present, colloidal or otherwise, may be considered to form a haked scaffolding from one wall of the container to the other, and during flow these links are

continually being broken and reformed. If the energy required to break a link is large compared with the thermal energy, the life of the link will be largely independent of thermal energy. Lubricating oils have long chain molecules which at very low rates of shear can be disentangled by thermal energy, whereupon the behaviour is Newtonian. At higher rates, however, the disentanglement is brought about by the shearing stress and hence the apparent viscosity decreases and the oil is thixotropic.

Some pastes, wet sand for example, exhibit *inverse thixotropy*, where the viscosity increases with increasing rate of shear. Many of these cases can be explained in terms of a separation of the phases, as in the example chosen, where the water is squeezed out between the sand particles which then show some of the properties of solid friction.

Any viscosity apparatus which permits easy change in the rate of shear can be used to demonstrate thixotropy and to amass useful empirical data. Qualitatively, the oscillating-disc method was early used; a rate of damping which decreases with increasing amplitude and velocity indicates thixotropy. Quantitatively, the rotating-cylinder method is excellent and Hatschek's viscometer (fig. 8) has been used for this purpose. As the linear velocity gradient at any radius r is given by $r \cdot d\omega/dr$, from equations (15) and (16) we have

$$r \frac{d\omega}{dr} = \frac{2\Omega}{r^2} \cdot \frac{a^2 b^2}{(b^2 - a^2)} \quad \dots \dots \dots (29)$$

It is possible to determine the velocity at any point directly by the insertion of a hot-wire anemometer, but this may disturb the stream-line flow. Alternatively, if the cylinder separation is small, taking the average of the extreme values, a mean rate of shear $\Omega(a^2 + b^2)/(b^2 - a^2)$ is obtained, and since η is given by (16), the variation of η with the rate of shear may be examined either by varying the rate of rotation of the moving cylinder or by using suspension wires of various kinds.

16. Special Plastometers.

The recognition of thixotropy, the wide range of numerical values of the viscosity coefficient for different materials, and the practical importance of the subject in metallurgy and the petroleum industry alone, have led to the development of many different types of viscometer and plastometer designed for special purposes. Even so, the standard methods already described are still widely used and recently Stokes's falling-sphere method has been further developed. For opaque liquids, the passage of the steel sphere past various points is determined from X-ray photographs, or alternatively by the induction effect as the sphere passes through coils wound on the fall tube.

The change in viscosity on stirring thixotropic fluids is easily measured by noting the time of fall of the same sphere before and after

stirring. For a given sphere the stress is constant but fresh material is being sheared continuously. Rate of shear can be varied by using spheres of different radii or different density. Holladay has modified the apparatus by replacing the gravitational field by that due to an electromagnet. With an iron sphere of microscopic size placed at various distances from the pole-piece, different rates of shear are developed, and the corresponding velocities are measured in a horizontal plane. In this way it has been shown that while substances like polymethyl methacrylate are generally non-Newtonian in behaviour, at sufficiently low rates of shear the behaviour is Newtonian and hence a representative value of η may be stated for such materials.

Finally, Stokes's method is suitable for very viscous fluids, an advantage possessed also by the rotating-cylinder method but less conspicuously by the capillary-flow method unless special means are adopted to apply forcibly a large pressure gradient. For exceptionally viscous fluids like pitch, Pochettino's apparatus shown diagrammatically in fig. 15 may be used. Two coaxial cylinders A and B are mounted with their common axis vertical; the space between is filled with the viscous liquid and the outer cylinder is held rigidly. Then neglecting the mass of the fluid compared with that of the inner cylinder and suspended mass W , if the latter descends with a constant velocity u , applying equation (1) we have

$$F = Wg = -\eta \cdot 2\pi l \frac{dv}{dr}$$

where l is the length of the cylinder. On integration and substitution

$$\eta = \frac{Wg}{2\pi lu} \log_e \frac{b}{a} \quad (30)$$

For accurate use the thickness of the annulus should be small compared with its length.

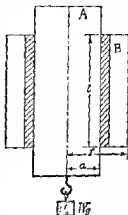


Fig. 15 - Pochettino's apparatus

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CHAPTER XIII

Errors of Measurement; Methods of Determining Planck's Constant

1. Introduction.

In making measurements which are intended to be as accurate as possible, the experimenter attempts to eliminate all the sources of error in his method. All sources of *systematic error* are first removed. If the readings are then taken with the highest possible precision, the uncertainty principle of Heisenberg asserts that uncertainties will still remain even if the observer and the apparatus are "perfect". A full discussion of this principle cannot be given here,* but it may be mentioned that uncertainties still remain in measurements of length, velocity, momentum, &c., even if the apparatus is "perfect". Other *accidental errors*, bigger than those just mentioned, arise in all measurements, because the personal judgment of the observer is employed, for example, to estimate the coincidence of two linear graduations, or of two events in time, or of analogous things, and the estimate made is always faulty to a greater or less degree. It is with these accidental errors that we are particularly concerned in this chapter. To deduce the "most accurate" value of a quantity from a set of experimentally measured values different methods are available, according as the quantity sought (a) is the quantity directly measured, (b) satisfies a linear relation, or (c) satisfies some other relation.

The theory of these methods is in many cases based on the Gaussian theory of errors. Although doubt has recently been thrown on the application of the theory to physical calculations, it is still accepted by most authorities.

2. The Gaussian or Normal Error-distribution Law.

Suppose that a large number n of experimental values of a single quantity, $x_1, x_2, x_3, \dots, x_n$, have been found, all of which are equally reliable and free from constant or systematic error. It may be shown

* See e.g. Born, *Atomic Physics* (Blackie, sixth edition, 1957)

on plausible grounds that the most accurate value x is that of the average or arithmetic mean, defined by $(x_1 + x_2 + \dots + x_n)/n$. Let the quantities $d_1 = x_1 - x$, $d_2 = x_2 - x$, &c., be calculated. The quantities d_1 , d_2 , &c., are called *residuals*, *deviations* or *divergences*. The total number of the residuals is equal to n , the total number of observations. Consider the number dn of residuals whose numerical value, independent of sign, lies between two limits z and $z + dz$. The Gaussian error-distribution law asserts that in *all* cases

$$dn = Ane^{-h^2z^2} dz, \quad \dots \dots \dots (1)$$

where A and h are constants

Since the total number of residuals equals n , and their possible range is from $z = 0$ to $z = \infty$,

$$\int_0^\infty dn = n = An \int_0^\infty e^{-h^2z^2} dz = \frac{An\sqrt{\pi}}{h}.$$

Hence $A = h/\sqrt{\pi}$ and

$$dn = nhe^{-h^2z^2} \frac{dz}{\sqrt{\pi}} \quad \dots \dots \dots (2)$$

The constant h is called the *Gaussian measure of precision* *. If h is large, the residuals are crowded more closely towards the value zero, if h is small, the residuals are spread over a large range. Thus h has different values for different sets of results.

Tests of the truth of the Gaussian error-distribution law include (a) one by Bessel, using 470 observations by Bradley, of a certain astronomical angle. There is very good agreement between the actual and Gaussian values of dn , in various ranges z to $z + dz$, except when z is very large. More large residuals are found experimentally than are predicted by theory. (b) Birge (1932) made 500 settings of a cross-wire on the centre of a wide spectrum line. The distribution of the residuals was in good agreement with the Gaussian law, even for large residuals. (c) Astronomical observations by Merriman, 300 in number, gave a strictly Gaussian distribution of residuals.

According to Campbell,† on the other hand, the Gaussian theory has for many years been held in such superstitious reverence that no effort has been made to accumulate data by which a decision might be made between Gaussian rules (of which the above is one) and possible alternatives. He agrees, however, that Gaussian rules lead in certain circumstances to permissible results, and that they have long been employed with apparent success.

A graph representing the normal or Gaussian law of error-distribution is shown in fig. 1.

* It must not be confused with Planck's constant of action, also denoted by h .

† *Measurement and Calculation*, pp. 163-163 (Longmans, 1928)

3. Measurement of a Single Quantity. Probable Error.

Suppose that a large number n of experimental determinations of a single quantity have been made. Let these be x_1, x_2, \dots, x_n . It is required to calculate the most accurate value of x given by the experiments.

Method I.—One convenient and permissible procedure is to arrange the n values of x_1, x_2 , &c., in ascending order, and if n is odd, simply select the middle quantity as the required "most accurate" value of x . This quantity is known as the *median*. If n is even, select the two middle values of x and find their mean.

Method II.—The usual method is to proceed as on p. 292 and find the average or arithmetic mean $x = (x_1 + x_2 + \dots + x_n)/n$. This is more laborious than Method I.

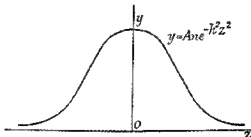


FIG. 1

Such a result is often stated thus: the most accurate value of the quantity sought is $x \pm a$. For example, Millikan announced his value of the electronic charge as $(4.774 \pm .004) \times 10^{-10}$ e.s.u. The symbol a usually, though not always, indicates a quantity known as the *probable error* or *dispersion* of the arithmetic mean. It is appended to x in order to give a quantitative estimate of the dispersion, range, or spread of the set of experimental investigations. If the values x_1, x_2, \dots, x_n are spread over a wide range, the precision of the measurements is not so great as if they are spread over a narrow range. In a large set of results, half of the errors exceed and half fall short of a certain quantity $\sqrt{n} a$. The probable error a is defined thus: it is a number such that the arithmetic mean x is just as likely to be in error by a number falling short of a as by a number exceeding a . Or, it is just as likely that the true value of x lies within the range of $x - a$ to $x + a$ as outside that range (sometimes referred to as the *fifty per cent zone*). Or, again, the odds that the true value lies within the range $x - 5a$ to $x + 5a$ are 1000 to 1, which is reckoned as a certainty. The quantity $5a$ is called the *maximum error*. In Millikan's case, the

probable error is 0.004, and the maximum error is $5 \times 0.004 = 0.02$, so that the odds are 1000 to 1 that the true value of e lies within the range $(4.751 - 4.791) \times 10^{-10}$ e.s.u. and not outside it.

According to the Gaussian theory of errors, the probable error is calculated as follows. Having obtained the arithmetic mean \bar{x} , we calculate the residuals $d_1 = x_1 - \bar{x}$, $d_2 = x_2 - \bar{x}$, &c., and then the sum $d_1^2 + d_2^2 + \dots + d_n^2 = \Sigma d^2$, say. Then

$$\alpha = .6745 \sqrt{\frac{\Sigma d^2}{n(n-1)}}, \quad \dots \dots (3)$$

where n is the total number of values.* The approximate value

$$\alpha = \frac{2}{3\pi} \sqrt{\Sigma d^2} \quad \dots \dots (4)$$

is sufficiently accurate for most purposes. The quantity $\pm \sqrt{\Sigma d^2/n}$ is called the *standard deviation* or *mean deviation* from the arithmetic mean. Thus the probable error is $2/3\sqrt{n}$ times the standard deviation. Another expression given by Gaussian theory for the probable error is

$$\alpha = \frac{.6453}{n} \frac{\Sigma d}{\sqrt{n-1}} = \frac{5}{6n} \frac{\Sigma d}{\sqrt{n}}, \text{ approximately.} \quad (5)$$

It appears that not all authors, when stating a result in the form $x \pm \alpha$, mean thereby that α is the probable error. Some authors intend α to mean the standard deviation †. It is therefore essential to find out exactly what each author means by the statement that his result is $x \pm \alpha$. Engineers dimension their drawings in the form $x \pm \alpha$, meaning by α the nominal dimension and by $\pm \alpha$ the tolerance or allowable margin of error either way.

4. Probable Error or Dispersion of a Single Observation.

After making the n observations x_1, x_2, \dots, x_n , suppose that one more observation is made. Where is it likely to lie? A quantity β , called the *probable error* or *dispersion* of a single observation, exists such that it is equally likely that the new value obtained differs from the true value by a quantity exceeding β as by a quantity falling short of β . Theory gives

$$\beta = \alpha \sqrt{n} \quad \dots \dots (6)$$

It can be shown that the probable error of α itself is $0.4769\alpha/n^{\frac{1}{2}}$, or, as is sometimes stated, the fractional probable error of α itself is $0.4769/n^{\frac{1}{2}}$.

* Proofs of formulæ (3), (5), and (6) are given in Whittaker and Robinson, *The Calculus of Observations*, pp. 205, 206 (Blackie, fourth edition, 1944).

† See remarks by Baker, *Proc. Phys. Soc.*, Vol. 45, p. 253 (1933).

5. The Weighting of Observations.

When more confidence can be placed in one measured quantity than in another, it is said to have more weight. The question arises, how is this to be taken into consideration quantitatively in calculating the most accurate value of a physical quantity from a set of experimental values?

Consider a case in which a large number of values x_1, x_2, \dots, x_n of a single quantity have been obtained by experiment, and suppose that if equal confidence could be placed in all the values the arithmetic mean would be chosen as the "most accurate" value of x . What is to be done if equal confidence cannot be placed in all the values? Some authors, e.g. Campbell,* say that observations should never be weighted. "The accuracy of a given set of observations, if they are sufficient in number, can never be improved by combining them with less accurate observations. If their number is insufficient it should be increased. . . . It is quite common to see a value for some important constant obtained by the combination of the results of many different workers, some of whose experiments were obviously less valuable than those of others. I can see no justification for this procedure; if the experiments that criticism shows to be the most trustworthy do not give a trustworthy result, then no trustworthy result is available."

While ideally it may be desirable to increase the number of accurate observations and reject all those of lesser precision, practical considerations of time and expense are by many authors considered to justify the inclusion of the more doubtful results, if they are given suitable weight.

One method, which is sometimes used but seems unsatisfactory, is to assign numerical integers w_1, w_2, \dots , to each quantity x_1, x_2, \dots respectively, basing the values of w_1, w_2, \dots on a purely intuitive estimate of the relative confidence to be placed in x_1, x_2, \dots . For example, in a certain case it might be considered that twice as much confidence could be placed in x_1 as in x_2 , or in x_3, \dots , and values $w_1 = 2, w_2 = 1, w_3 = 1, \dots$ might be assigned to x_1, x_2, x_3, \dots respectively. These numbers w_1, w_2, \dots are called the *weights* of x_1, x_2, \dots respectively. In the general case, after the weights are assigned, a quantity

$$x = \frac{w_1 x_1 + w_2 x_2 + \dots}{w_1 + w_2 + \dots}, \quad \dots \quad (7)$$

called the *weighted mean*, is calculated.

Another procedure is to combine results obtained by different observers as follows. A certain observer announces the result of his

* *Measurement and Calculation*, p. 167.

measurements of a certain quantity as $x_1 \pm a_1$; another investigator gives his result for the same quantity as $x_2 \pm a_2$, a third as $x_3 \pm a_3$, and so on. Assume that a_1, a_2, \dots are the respective probable errors of the arithmetic means. To combine these results, begin by calculating the weights w_1, w_2, \dots of the different results, which on Gaussian theory are given by $w_1 = 1/a_1^2, w_2 = 1/a_2^2$, and so on. The final most accurate value of x is taken to be

$$x_m = \frac{w_1 x_1 + w_2 x_2 + \dots}{w_1 + w_2 + \dots} = \frac{x_1/a_1^2 + x_2/a_2^2 + \dots}{1/a_1^2 + 1/a_2^2 + \dots}, \quad (8)$$

which can be written in the form

$$x_m = \frac{\sum w x}{\sum w}, \quad (9)$$

$$\text{and } \delta_1 = x_1 - x_m, \quad \delta_2 = x_2 - x_m, \quad \dots$$

equal to unity, except for statistical fluctuations. Here $\delta_1 = x_1 - x_m, \delta_2 = x_2 - x_m, \dots$ where x_m is the weighted mean, as in equation (8), w_1, w_2, \dots are the weights $1/a_1^2, 1/a_2^2, \dots$ respectively, $\sum w \delta^2 = w_1 \delta_1^2 + w_2 \delta_2^2 + \dots$, and N is the number of independent sets of results which are to be combined. Provided that Z does not differ from unity by a quantity exceeding $0.4769/N^{1/2}$, the combination of results is permissible. If Z differs from unity by five times $0.4769/N^{1/2}$, there is only one chance in a thousand that such a deviation is due to mere statistical fluctuation, that is, the odds are 999 to 1 that constant or systematic errors are present in one or more sets of results, and it is not permissible to combine them.

It may be shown that the value of the weighted mean x_m , given by equation (8), has a probable error

$$a = 0.6745 \{ \sum w \delta^2 / (N - 2) \sum w \}^{1/2},$$

where the symbols have the meanings just given.

6. Calculation of the Constants in the Linear Law $y = mx + c$.

Suppose that it is known that "exact" values of two quantities, x and y , obey a linear law of the form $y = mx + c$. Suppose also that a large number of pairs of values of x and y have been obtained experimentally. It is required to find the "most accurate" values of m and c , the constants in the equation. If exact values of x and y were available, two pairs of them, x_1, y_1 , and x_2, y_2 , would be sufficient to determine exact values of m and c . As, however, the values available are only experimental, another procedure must be adopted. Various methods are regarded as permissible.

(i) *Graphical Method*.—A graph connecting x and y is plotted, each point being plotted immediately after each single pair of observations is made. The straight line which lies most evenly among these points is determined by a black thread or a transparent celluloid rule with a central straight line engraved upon it. Immediate plotting reduces the number of observations needed. The most accurate values of m and c are given by the tangent of the angle of slope and the intercept on the y -axis respectively. The accuracy of this method is limited, because there are practical limits to the accuracy with which an angle or a length can be measured. The accuracy is also affected by the scale of the graph, a large scale being better than a small one.

(ii) *Method of Zero Sum* (Mayer's or Campbell's Method).—In making the experiments, one of the two quantities x and y is usually arranged or set at some value, the other being allowed to come as it may. For example, in measuring the coefficient of linear expansion of a rod, the temperature may be set at definite values, and the length allowed to come as it may. The present method of obtaining the most accurate values of m and c is as follows.

Arrange the values of the set quantity, which may be taken as x , in ascending order of magnitude, x_1, x_2, x_3, \dots . Write down equations in the order $y_1 = mx_1 + c, y_2 = mx_2 + c, \dots$. Suppose that in all there are n equations. If n is even, add the first $n/2$ equations together, obtaining a single "normal" equation of the form $Y_1 = mX_1 + nc/2$, where $Y_1 = y_1 + y_2 + \dots + y_{n/2}$ and $X_1 = x_1 + x_2 + \dots + x_{n/2}$. Add the second group of $n/2$ equations together, obtaining a second normal equation of the form $Y_2 = mX_2 + nc/2$. Then solve this pair of simultaneous normal equations for m and c in the ordinary way. We get

$$m = \frac{Y_1 - Y_2}{X_1 - X_2},$$

$$c = \frac{2(X_1Y_2 - X_2Y_1)}{n(X_1 - X_2)}. \quad \dots \dots (10)$$

If n is odd, add the first $(n-1)/2$ equations to the next equation (the middle one of the set), multiplied throughout by $1/2$, to get a single normal equation. Add the middle equation multiplied by $1/2$ to the remaining $(n-1)/2$ equations to get a second normal equation. Then solve the two normal equations for m and c in the usual way.

The arithmetic of this method is fairly quick, but it gives different values of m and c according to which of the two experimental quantities we "arrange" or "set".

✓(iii) *Gaussian Method of Least Squares*.—The deviation of any two observed values x_1, y_1 from the straight line $y = mx + c$ may be written as $d_1 = c + mx_1 - y_1$. For several pairs of readings, the

method of least squares states that the best representative values of m and c are those for which the sum of the squares of the deviations is least; to find these values we proceed as follows.

Take the first of the set of n equations, namely, $y_1 = mx_1 + c$. Multiply it by the coefficient of m , i.e. by x_1 , which gives $x_1 y_1 = mx_1^2 + cx_1$. Repeat with all the n equations and add; this gives $X_1 Y_1 = mX_1^2 + cX_1$, where $X_1 Y_1 = \sum xy$, $X_1^2 = \sum x^2$, and $X_1 = \sum x$. Next take the first equation and multiply it by the coefficient of c , which happens to be unity; this simply gives $y_1 = mx_1 + c$. As the coefficient of c in every equation is unity, simply add the n equations as they stand, this gives $Y_1 = mX_1 + nc$, where $Y_1 = \sum y$. Solve the two normal equations thus obtained for m and c ; this gives

$$m = \frac{nX_1 Y_1 - Y_1 \cdot X_1}{nX_1^2 - X_1 \cdot X_1}, \quad \checkmark \quad \dots \quad (11)$$

$$c = \frac{X_1^2 \cdot Y_1 - X_1 \cdot X_1 Y_1}{nX_1^2 - X_1 \cdot X_1} \quad \dots \quad (12)$$

The probable errors of the values of m and c obtained by the method of least squares, equal weights being assumed for every pair of values of x and y , may be shown to be

$$\sigma_m = 0.6745 \left\{ \frac{n \Sigma \delta^2}{(n-2)(nX_1^2 - Y_1 \cdot X_1)} \right\}^{\frac{1}{2}} \checkmark$$

and

$$\sigma_c = 0.6745 \left\{ \frac{\Sigma \delta^2 \cdot X_1^2}{(n-2)(nX_1^2 - Y_1 \cdot X_1)} \right\}^{\frac{1}{2}} \checkmark$$

Here X_1 and X_1^2 have their previous meanings. Each δ is calculated as follows. In the equation $y = mx + c$ we use the calculated values of m and c , derived from equations (11) and (12), and, in turn, insert the set values x_1, x_2, \dots , and calculate values of y , which may be called y'_1, y'_2, \dots . Then δ_1 is the difference between the calculated value y'_1 and the experimental value y_1 , or $\delta_1 = y'_1 - y_1$. $\delta_2 = y'_2 - y_2, \dots$. Hence $\Sigma \delta^2 = (y'_1 - y_1)^2 + (y'_2 - y_2)^2 + \dots$.

The arithmetic in this method is usually somewhat laborious, though the use of modern calculating machines reduces the labour considerably. The method has the advantage of giving the same result no matter which quantity is "arranged" or "set" at definite values. It is not now regarded as having any better theoretical justification than other methods, but is classed along with others as a possible method.

(iv) *Cauchy's (or Averbey's) Method.*—This method has the advantage of involving much less arithmetical labour than that of least squares. Suppose that n pairs of observations $y_1, y_2, \dots, y_n, x_1, x_2, \dots, x_n$

have been made. As before, the law is known to be of the form $y = mx + c$. Its graph is a straight line. Find a point X, Y which may be called the centroid of all the points, i.e. find $X = \Sigma x/n$, $Y = \Sigma y/n$. Next, divide the n values into two sets as follows. Let i of them have values of x less than X , the other $n - i$ having values of x greater than X . Find the centroid of the i values such that $x < X$, i.e. find $\Sigma x/i$ and $\Sigma y/i$ for these i values. Let $\Sigma x/i = X_1$ and $\Sigma y/i = Y_1$. Also find the centroid of the remaining $n - i$ values, for which let $\Sigma x/(n - i) = X_2$ and $\Sigma y/(n - i) = Y_2$. Assume that the best value of m is $(Y_2 - Y_1)/(X_2 - X_1)$, which is the slope of the straight line joining the points (X_1, Y_1) , (X_2, Y_2) on a graph. Assume that the best value of c is the value of c given by putting $Y = mX + c$, i.e. $c = Y - mX$, where (X, Y) is the centroid of all the points and $m = (Y_2 - Y_1)/(X_2 - X_1)$.

7. Probable Error of a Function of Quantities Measured Experimentally.

The values of many physical quantities are calculated by substituting experimental values of various measurable quantities in a formula; for example, the viscosity of a liquid is calculated from Poiseuille's formula $\eta = \pi p a^4 / 8 Q l$ (p. 273). All the quantities p, a, Q, r, t , and l are measured in some way. The value of each has its own probable error. What is the probable error of the result that is obtained for η ?

To put this in more general terms, if a quantity Z is a function of x, y, z, \dots , and if the probable error of x is $\pm a_1$, of y , $\pm a_2$, of z , $\pm a_3, \dots$, what is the probable error a of the value of Z obtained by calculating $f(x, y, z, \dots)$? Theory indicates that

$$a^2 = \left(\frac{\partial f}{\partial x} \right)^2 a_1^2 + \left(\frac{\partial f}{\partial y} \right)^2 a_2^2 + \dots$$

where $\partial f / \partial x$ means the partial derivative of $f(x, y, z, \dots)$ with respect to x when y, z, \dots are treated as constants, and so on.

For example, the volume V of a cone is $\pi r^2 H / 3$. Let the probable errors of r and H be a_1 and a_2 respectively. Since $V = \pi r^2 H / 3$, $\partial V / \partial r = 2\pi r H / 3$ and $\partial V / \partial H = \pi r^2 / 3$. Hence $a^2 = 4\pi^2 r^2 H^2 a_1^2 / 9 + \pi^2 r^4 a_2^2 / 9$. Other exercises for solution are given on p. 318.

8. Determination of Planck's Constant.

The determination of the most reliable value for Planck's constant of action h by Bond and by Birge, which is described later, affords a good example of the application of the method of least squares. The description of Bond's work is preceded by a short account of the other main methods of determining h . It has been found necessary to assume a fair knowledge of sub-atomic physics on the part of the student.

since proofs of the various formulae used would lead us beyond the scope of this book.*

9. Method based on Bohr's Theory of Atomic Structure.

According to Bohr's theory of atomic structure,

$$R_{\infty} = \frac{2\pi^2 e^5}{h^3 c^2 (e/m)}$$

where R_{∞} is the Rydberg constant for infinite mass, and its units are cm.^{-1} , e is the electronic charge in absolute c.s.u., and e/m is in absolute e.m.u. Further,

$$R_{\infty} = R_H \left(1 + \frac{m}{m_H} \right), \quad \checkmark$$

where R_H is the observed Rydberg constant for hydrogen, m is the rest-mass of an electron, and m_H the mass of the nucleus of a hydrogen atom, that is, of a proton.

This may also be written in the form

$$R_{\infty} = R_H \left\{ 1 + \frac{F}{(H - m)Ne/m} \right\},$$

where F is the value of the electric charge associated in electrolysis with one gramme-equivalent of any ion, in absolute e.m.u., that is, the value of the faraday in e.m.u., H is the mass of a hydrogen atom in grammes, and N is Avogadro's number. Hence, since

$$h^3 = \frac{2\pi^2 e^5}{R_{\infty} c^2 (e/m)},$$

we have

$$h = \left[\frac{2\pi^2 e^5}{c^2 (e/m) R_H \left\{ 1 + \frac{F}{(H - m)(e/m)} \right\}} \right]^{1/3}. \quad (13)$$

10 Ionization Potential Method.

The ionization potential most accurately determined hitherto is that of mercury by Lawrence.† The excitation potentials most accurately determined are those of certain lines in the spectra of helium, neon and argon by (a) van Atta (1931), and (b) Whiddington and Woodroffe (1935). The values are stated in international volts ($= V'$, say). To reduce V' to absolute c.s.u. of potential difference, it is not permissible simply to divide by 300. Allowance must be made for the fact that the international volt is 1.00033 absolute volts and that e ,

* See e.g. Wilson, *Modern Physics* (Blackie, third edition, 1946); Born, *Atomic Physics* (Blackie, sixth edition, 1967).

† *Phys. Rev.*, Vol. 28, p. 947 (1928).

the velocity of light in *vacuo*, is 2.99776×10^{10} cm. per sec. The relation between h and the ionization or excitation potential, measured in absolute e.s.u. of potential difference, is

$$h\nu = eV$$

or

$$h = \frac{eV}{\nu} = \frac{e\lambda V}{c},$$

where λ is the wave-length corresponding to the ionization potential of mercury; e and V are in absolute e.s.u., ν in vibrations per second, and λ in cm. As

$$V = \frac{V' \times 1.00033 \times 10^8}{c},$$

$$h = \frac{e\lambda V' \times 1.00033 \times 10^8}{c^2}. \quad . \quad . \quad . \quad (14)$$

11. X-ray Continuous-spectrum Method.

This method is analogous to the last, but makes use of X-rays. If the intensity wave-length diagram of the continuous X-ray spectrum of any anticathode is examined, it is found that the point where the curve cuts the wave-length axis is constant, no matter what the nature of the anticathode is, provided the applied potential is constant. It is assumed that the corresponding frequency of the X-ray beam is connected with the full applied potential V by the relation

$$h\nu = \frac{hc}{\lambda} = eV, \quad . \quad . \quad . \quad . \quad (15)$$

or

$$h = \frac{\lambda eV}{c}, \quad . \quad . \quad . \quad . \quad (16)$$

Here V and e are in absolute e.s.u., λ in cm. and c in cm. per sec. In this case λ is measured by regular reflection from a calcite crystal, using Bragg's law, namely, $\lambda = 2d \sin \theta$, where d is the lattice constant of the crystal.

Hence

$$h = \frac{2eVd \sin \theta}{c}$$

or

$$h = \frac{2eV'd \times 10^8 \times \sin \theta \times 1.00033}{c^2}, \quad . \quad . \quad . \quad (17)$$

where V' is the potential applied to the X-ray tube in international volts,

12. Photoelectric Method.

In this method use is made of Einstein's law, namely,

$$Ve = h\nu - P, \quad \dots \quad (18)$$

which connects P , the work required to extract an electron from a metal, with V , the retarding potential, and ν , the frequency of the incident radiation. On differentiating and rearranging, we have

$$\frac{\partial V}{\partial \nu} = \frac{h}{e}. \quad \dots \quad (19)$$

In the accurate work of Lukirsky and Frlenzev (1928), the critical potential V' , at which light of frequency ν sets up electron emission from a metal, is measured for a large number of values of ν , and for several metals. A graph connecting V' and ν is plotted. Its slope gives $\partial V'/\partial \nu$.

As before, the potential as measured is V' international volts, and $V = V' \times 1.00033 \times 10^8/e$ e.s.u. Then

$$\frac{h}{e} = \frac{\partial V}{\partial \nu} = \frac{1.00033 \times 10^8}{e} \frac{\partial V'}{\partial \nu}$$

and

$$h = \frac{1.00033 \times 10^8 \times e \partial V'}{\partial \nu} \quad (20)$$

In a second and more accurate photoelectric method used by Robinson and his co-workers, X-rays replace visible light. Monochromatic X-rays of known frequency fall on a thin film or target and eject photoelectrons. The kinetic energy of such an electron is equal to the energy of a quantum $h\nu$ of the incident energy of the X-rays minus the work of extraction $h\nu_0$. Thus

$$h(\nu - \nu_0) = \frac{1}{2}mv^2.$$

On applying a uniform magnetic field of strength H normal to the direction of motion of an electron, it describes a circle of radius ρ given by

$$Hecv = \frac{mv^2}{\rho} \quad \text{and} \quad v = \frac{Hec\rho}{m}.$$

Eliminating v from these equations and solving for h , we get

$$h = \frac{2m(\nu - \nu_0)}{e^2\rho^2H^2}.$$

13. Wien's Displacement Law Method.

It follows from Wien's displacement law concerning full or black-body radiation that *

$$\lambda_{\max} \theta = \text{a constant} = \frac{hc}{k\beta} \quad (21)$$

where λ_{\max} is the wave-length corresponding to the peak of one of Planck's spectral distribution curves, θ is the temperature of the full radiator concerned, k is Boltzmann's constant, and β is the positive root of the equation

$$e^{\beta} + \frac{\beta}{5} - 1 = 0; \quad (22)$$

$\beta = 4.8651$ to four places of decimals. Hence

$$\begin{aligned} h &= \beta k \lambda_{\max} \frac{\theta}{c} \\ &= \beta R \lambda_{\max} \frac{\theta}{Nc} \quad (23) \end{aligned}$$

where R is the universal constant for one gramme-molecule of a perfect gas and N is the number of molecules in a gramme-molecule. Among the quantities present in this equation N is the one whose value is known least accurately, its value being given by the relation $Nc = F$, where F is defined as in equation (13). p. 309.

14. Stefan's Law Method.

Stefan's fourth-power law † may be stated as $E = \sigma \theta^4$, where E is the total energy contained in rays of all wave-lengths emerging from an aperture in the walls of a full radiator per sq. cm. per sec., θ is the absolute temperature of the full radiator, and σ is a measurable constant. Further, h is connected with σ by the relation

$$h = \left(\frac{2\pi^5 k^4}{15c^2 \sigma} \right)^{1/3} \quad (24)$$

Perhaps the most accurate value of σ yet obtained is that of Hoare (1928), namely, $\sigma = 5.735 \times 10^{-8}$ erg cm.⁻² deg.⁻⁴ sec.⁻¹. The quantity c is introduced through Boltzmann's constant $k = R/N = R_e/F$.

15. Eddington's Fine-Structure Constant Method.

According to a theory of Eddington (1929), based on the wave equation for two electrons of like spin,

$$\frac{hc}{2\pi e^2} = \frac{1}{\alpha}$$

* Roberts, *Heat and Thermodynamics*, fourth edition, p. 432.

† *ibid.*, p. 472.

where α is a pure number, now called the *Sommerfeld fine-structure constant*. The latest value of α , as calculated by Du Mond (1949) is $137.027 \pm .007$, a value very near the integer 137. α is obtained by a combination of experiment and calculation, as follows. According to Fermi's hyperfine-structure formula (1930), neglecting certain corrections, the frequency ν corresponding to the hyperfine-structure separation of the ground state of a hydrogen atom, is given by

$$\nu = \frac{\alpha^2 \cdot 16\mu_p R_\infty}{3\mu_e},$$

where μ_p and μ_e are the magnetic moments of the proton and electron, respectively. Hence from the last two equations we get

$$h = \frac{2\pi c^2}{\alpha c} = 8\pi c^2 \left\{ \frac{\mu_p R_\infty}{3\mu_e c} \right\}^{1/2}.$$

16. Electron Diffraction Method (Velocity obtained from the Accelerating Potential).

In this method as used by von Friesen (1933), electrons accelerated by a known voltage are diffracted by a crystal of galena. The de Broglie waves associated with the electron obey Bragg's law. Their wavelength λ is given by $\lambda = h/mv$, so that

$$h = \lambda mv, \text{ where } v \text{ is the velocity.}$$

Hence
$$h = \frac{\lambda m_0 v}{\sqrt{1 - v^2/c^2}} \text{ by relativity theory}$$

and
$$\frac{h^2}{\lambda^2 m_0^2} = \frac{v^2}{1 - v^2/c^2}.$$

Hence
$$\frac{h^2}{\lambda^2 m_0^2 c^2} = \frac{v^2/c^2}{1 - v^2/c^2}$$

and
$$1 + \frac{h^2}{\lambda^2 m_0^2 c^2} = 1 + \frac{v^2/c^2}{1 - v^2/c^2} = \frac{1}{1 - v^2/c^2}. \quad (25)$$

Now the kinetic energy of an electron, produced by an accelerating potential V , is

$$mc^2 - m_0 c^2 = Ve.$$

Hence
$$\frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} - m_0 c^2 = Ve,$$

so that
$$\frac{1}{1 - v^2/c^2} = \left(\frac{Ve + m_0 c^2}{m_0 c^2} \right)^2. \quad (26)$$

Comparing equations (25) and (26) it is seen that

$$1 + \frac{h^2}{\lambda^2 m_0^2 c^2} = \left(\frac{Ve + m_0 c^2}{m_0 c^2} \right)^2 = \left(1 + \frac{Ve}{m_0 c^2} \right)^2.$$

Hence

$$\begin{aligned}\frac{h^2}{\lambda^2 m_0^2 c^2} &= \left(1 + \frac{Ve}{m_0 c^2}\right)^2 - 1 \\ &= \frac{2Ve}{m_0 c^2} + \left(\frac{Ve}{m_0 c^2}\right)^2 \\ &= \frac{2Ve}{m_0 c^2} \left(1 + \frac{Ve}{2m_0 c^2}\right),\end{aligned}$$

so that

$$h^2 = \lambda^2 \cdot 2Vem_0 \left(1 + \frac{Ve}{2m_0 c^2}\right)$$

and

$$h = \lambda(2Vem_0)^{1/2} \left(1 + \frac{Ve}{2m_0 c^2}\right)^{1/2}.$$

λ can be written as $(2d \sin \theta)/n$ by Bragg's law, so that finally

$$h = \frac{2d \sin \theta (2Vem_0)^{1/2}}{n} \left(1 + \frac{Ve}{2m_0 c^2}\right)^{1/2}.$$

The lattice constant d of the crystal is measured by X-rays in the usual manner.

17. Electron Diffraction Method (Velocity Measured Directly).

The special feature in this method, namely, the measurement of the velocity of electrons by a kinematic method, was proposed by Des Coudres (1897) and developed by Wiechert (1899), Kirehner (1924 and onwards) and Guan (1934). It is again assumed that electrons moving with a velocity v have a de Broglie wavelength λ given by

$$\lambda = h/mv \quad \text{and} \quad h = \lambda mv.$$

As before, λ is measured by a crystal diffraction experiment and $\lambda = (2d \sin \theta)/n$. The velocity v is measured in the following way.

A narrow parallel beam of electrons, all travelling at speeds lying within a very narrow range around v , passes in succession through the spaces between the plates of two small parallel-plate condensers, a certain distance s apart, and then falls on the slit of a suitable detector. The two condensers are connected in the same oscillatory circuit, and the potentials of corresponding plates of the two condensers are equal to each other at any instant. When the time interval taken by an electron to traverse the distance s from the first to the second condenser is exactly equal to one half-period ($\frac{1}{2}T$) of the oscillations, the resultant lateral deflection of the electron in the two condensers is zero. The electron beam, undeflected, falls on the unmoved slit of the detector. This is repeated when the time taken is any odd integral number of half-periods, say n' half-periods. In this case

$$v = \frac{s}{\frac{1}{2}n'T} = \frac{2s}{n'T} = \frac{2vs}{n'}, \quad \text{where } \nu \text{ is the alternating-current frequency.}$$

Finally, then, the equation

$$h = \lambda m v \quad \checkmark$$

becomes

$$h = \frac{2d \sin \theta}{n} \cdot \frac{m_0}{(1 - v^2/c^2)^{1/2}} \cdot \frac{2v}{\lambda'}$$

or

$$h = \frac{2d \sin \theta}{n} \left[\frac{m_0}{1 - 4v^2/c^2} \right]^{1/2} \frac{2v}{\lambda'}$$

using Bragg's law and the relativistic law of variation of mass with velocity.

18. Compton Shift Method.

The Compton effect is concerned with the change in wavelength $\Delta\lambda$ of a beam of X-rays, of wavelength λ , when scattered through an angle θ by impinging upon atomic electrons in a gas or solid. Older theory gives the expression

$$\Delta\lambda = \frac{h(1 - \cos \theta)}{mc} \quad (27)$$

The newer theory of Ross and Kirkpatrick (1934) takes into account the energy binding the scattering electron to its nucleus, and affirms that

$$\Delta\lambda = \frac{h(1 - \cos \theta)}{mc} - \frac{\lambda^2(1 - n)E}{\hbar c a} \quad (28)$$

where E is the binding energy and n is a numerical factor, whose value depends on the kind of motion described by the electron during expulsion. If a uniform acceleration is assumed, $n = \frac{1}{2}$, and

$$\Delta\lambda = \frac{h(1 - \cos \theta)}{mc} - \frac{\lambda^2 E}{\hbar c} \quad (29)$$

Hence, in this case, $(1 - \cos \theta)h^2 - mc \cdot \Delta\lambda \cdot h + m \cdot \lambda^2 E = 0$, a quadratic, and solving for h we get

$$h = \frac{mc \cdot \Delta\lambda \pm \{(mc\Delta\lambda)^2 - 4m\lambda^2 E(1 - \cos \theta)\}^{1/2}}{2(1 - \cos \theta)} \quad (30)$$

Ross and Kirkpatrick have measured $\Delta\lambda$ for three different values of λ , using the electrons in solid (a) carbon, (b) beryllium, as scatterers. The second term on the right of equation (30), when $n = \frac{1}{2}$, is about 1.3 per cent of the first term in value.

19. Bond's Method.

Having noticed that the various formulae connecting h and e can be written generally as a power formula

$$h = A e^a, \quad \checkmark \quad (31)$$

where A_n and n are constants, Bond (1930 and 1931) used the method of least squares in conjunction with 36 sets of independent results to find the most accurate value of A_n , n being given, and thence the most accurate values of h and e . As presented by Birge, the method is as follows.

Write equation (31) in the form

$$A_n = he^{-n}, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This is of the form $A_n = f(h, e) = he^{-n}, \quad . \quad . \quad . \quad . \quad . \quad (33)$

Let e_0, h_0 be any pair of known values of e and h which are known to be not far from the true values. Write

$$e = e_0 + \Delta e, \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$h = h_0 + \Delta h, \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Apply Taylor's theorem, namely,

$$f(h, e) = f(h_0, e_0) + \left(\frac{\partial f}{\partial h}\right)_{h=h_0} \Delta h + \left(\frac{\partial f}{\partial e}\right)_{e=e_0} \Delta e + \text{negligible terms.}$$

Now

$$\left(\frac{\partial f}{\partial h}\right)_{h=h_0} = e_0^{-n}, \quad \left(\frac{\partial f}{\partial e}\right)_{e=e_0} = -nh_0e_0^{-(n+1)}, \quad f(h_0, e_0) = h_0e_0^{-n}.$$

Hence $f(h, e) = A_n = h_0e_0^{-n} + e_0^{-n}\Delta h - nh_0e_0^{-(n+1)}\Delta e. \quad (36)$

Introduce a new parameter $h_n \equiv A_n e_0^n$, i.e. insert $A_n = h_n e_0^{-n}$ in (36). When reduced to the simplest form, equation (36) becomes

$$h_n = h - \left(\frac{h_0 \Delta e}{e_0}\right)n, \quad . \quad . \quad . \quad . \quad . \quad (37)$$

which is of the form $y = c + mx$, where $y = h_n$, $c = h$, $m = -h_0 \Delta e / e_0$, $x = n$.

The 36 observations included 14 values of h_n corresponding to $n = 3/3$, 9 values of h_n corresponding to $n = 4/3$, and 13 values of h_n corresponding to $n = 5/3$. When each of the 14 observations was given equal weight, the arithmetic mean value of h_n derived from them was 6.5473×10^{-27} ; the 9 values gave $h_n = 6.5364 \times 10^{-27}$, and the 13 values gave $h_n = 6.5395 \times 10^{-27}$. The problem to be solved was then as follows.

Given three equations

$$6.5473 \times 10^{-27} = h - (h_0 \Delta e / e_0) 3/3,$$

$$6.5364 \times 10^{-27} = h - (h_0 \Delta e / e_0) 4/3,$$

$$6.5395 \times 10^{-27} = h - (h_0 \Delta e / e_0) 5/3,$$

to find the most accurate values of h and $h_0\Delta e/e_0$ and hence of e by the method of least squares. The first equation was given the weight 14, the second 9, and the third 13, since the equations were based on 14, 9 and 13 values respectively.

Now when it is required to find the constants in the equation $y = mx + c$, given values x_1y_1 of weight w_1 , x_2y_2 of weight w_2 , x_3y_3 of weight w_3 , . . . , the method of least squares (p. 298) gives

$$c = \frac{\sum w_1 y_1 \sum w_1 x_1^2 - \sum w_1 x_1 \sum w_1 y_1}{\sum w_1 \sum w_1 x_1^2 - (\sum w_1 x_1)^2} \quad \dots \quad (38)$$

and

$$m = \frac{\sum w_1 \sum w_1 x_1 y_1 - \sum w_1 x_1 \sum w_1 y_1}{\sum w_1 \sum w_1 x_1^2 - (\sum w_1 x_1)^2}, \quad \dots \quad (39)$$

with a probable error in c of

$$0.6745 \left(\frac{\sum w_1 \delta^2}{n-2} \right)^{1/2} \left\{ \frac{\sum w_1 x_1^2}{\sum w_1 \sum w_1 x_1^2 - (\sum w_1 x_1)^2} \right\}^{1/2},$$

and a probable error in m of

$$0.6745 \left(\frac{\sum w_1 \delta^2}{n-2} \right)^{1/2} \left\{ \frac{\sum w_1}{\sum w_1 \sum w_1 x_1^2 - (\sum w_1 x_1)^2} \right\}^{1/2}.$$

Here $n = 3$ and δ is the deviation of each of the three values of h_0 given above from that calculated with the values of c and m calculated from equations (38) and (39).

Using Bond's data and these equations, Burge obtained $h_0\Delta e/e_0 = (0.0119 \pm 0.0071) \times 10^{-27}$, and using $h_0 = 6.547 \times 10^{-27}$ and $e_0 = 4.770 \times 10^{-10}$ e.s.u., he obtained

$$h = (6.5575 \pm 0.0096) \times 10^{-27}, \quad e = (4.7787 \pm 0.0052) \times 10^{-10} \text{ e.s.u.}$$

The value of e here obtained was independent of that obtained by Millikan's oil-drop method, which does not involve h . By taking the oil-drop result into account as well, by adopting what he believed to be the best arbitrary system of weighting, by using the most accurate results available in 1932, and by applying a method of calculation resembling the one just described, Burge obtained as his values

$$h = (6.5442 \pm 0.0091) \times 10^{-27}, \quad e = (4.7677 \pm 0.0010) \times 10^{-10} \text{ e.s.u.}$$

By way of comparison, the values of h and e computed by Burge in 1911, using more accurate later data than those of 1923, may be quoted. They are:

$$h = (6.6242 \pm .0024) \times 10^{-27} \text{ erg. sec.},$$

$$e = (4.8025 \pm .0011) \times 10^{-10} \text{ e.s.u.}$$

Du Mond and Cohen have introduced a powerful and interesting new method of calculating physical constants. It involves both the method of least squares and a geometrical figure called an isometric consistency chart. Inspection of this diagram reveals the consistency or want of it in data obtained by different experimental methods, and suggests which method is likely to contain hidden sources of error. Using the data available in 1949, the method gives $h = (6.6237 \pm .0011) \times 10^{-27}$ erg sec., $e = (4.8024 \pm .0005) \times 10^{-10}$ e.s.u.

20. Present Values of the Atomic Constants.

It will be clear that the atomic constants are continually being re-evaluated. Calculations have recently been made by Cohen, Du Mond, Layton and Rollett (1955) from the following point of view. They regard the numerical values of a certain number of physical quantities as known to a high degree of accuracy; these are called the *auxiliary fixed constants*. They include the Rydberg wave number, the velocity of light, the atomic masses of hydrogen, deuterium, the neutron and the proton, the gas constant per gm.-mol. and a few others. Four quantities, e the electronic charge, N Avogadro's number, α the fine structure constant, and λ the factor which converts X-ray wave-lengths measured in Siegbahn's α units into milliangstroms, are then regarded as primary unknowns to be evaluated. Various experimental researches provided eleven equations each of the form $e^i N^j \alpha^k \lambda^l = \text{constant}$, the indices i, j, k and l being known pure numbers. Each of the eleven equations was first linearized, that is reduced to an equation of the first degree as discussed on p. 307, when passing from equation (32) to equation (37). They were then subjected to an *analysis of variance*. Thus they were grouped into seven kinds, each kind determining a particular linear combination of the unknowns. There was only one equation of the first four kinds, two equations of each of the next two kinds, and three equations of the last kind. A sub-set of seven equations was then selected, including one equation of each kind, but not more than one. Of the many possible sub-sets of the seven equations, 171 were chosen from which to evaluate e, N, α and λ . The method of least squares was then used, the actual computation being done by the aid of an Electrodata Datatron Digital Computer. Each sub-set of seven equations gave a set of "adjusted" values of e, N, α and λ . A quantity termed the measure of consistency of the obtained values, denoted by χ^2 , was found for each sub-set, and that sub-set for which χ^2 was nearest the theoretically expected value, was regarded as giving the most reliable adjusted values of e, N, α and λ . The first published values were

$$e = (4.80286 \pm 0.00009) \times 10^{-10} \text{ e.s.u.}$$

$$N = (6.02486 \pm 0.00016) \times 10^{23} \text{ (gm.-mol.)}^{-1}$$

$$\alpha = (7.29729 \pm 0.00003) \times 10^{-3}, \quad 1/\alpha = 137.0373 \pm 0.0006$$

$$\lambda = 1.002639 \pm 0.000014$$

From these values, other quantities could be determined, for example $h = 2\pi\epsilon^2/ac = (6\ 62517 \pm 0\ 00023) \times 10^{-27}$ erg. sec. A corollary to these calculations was that if the inclusion of one equation raised the χ^2 value of a sub-set of seven equations more than the inclusion of another equation, the physical method on which the former equation was based probably contained one or more sources of undetected systematic errors. The suspected method was then more carefully considered regarding the sources of systematic errors.

Comparison of the values given in this section with those quoted at the end of § 19 shows that the value for e has changed by only two in the fourth decimal place. Further similar small changes will probably be made from time to time, it is already known that the value of λ quoted above requires a further small correction due to the discovery of the so-called Lamb shift of spectral lines which is attributed to polarization of a vacuum in the presence of an electric field.

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EXAMPLES

CHAPTER I

1. Determine the time of oscillation of a **drop of liquid** under surface-tension forces.
2. Obtain Poiseuille's equation for the volume of viscous liquid flowing per second through a cylindrical tube of circular cross-section.
3. Find by dimensional methods how the viscous force of resistance to the fall of a sphere under gravity depends on the radius of the sphere, its terminal velocity, and the coefficient of viscosity of the fluid through which it is moving.
4. Show that the quantity of heat H , lost per unit length per second per degree temperature excess from a long cylinder of diameter d submitted to forced convection in a fluid of thermal conductivity K , thermal capacity per unit volume c , kinematic viscosity ν , moving with relative velocity u , is given by $H/K = F(cu d/K) \cdot f(c\nu/K)$.
5. Determine the rate of radiation of energy from an accelerated electron.
6. Show that if the linear dimensions of the entire apparatus used in determining G by a torsion balance (see Chapter III, p. 41) are changed, the sensitiveness of the apparatus remains unaltered.
7. Show that the dimensions of D , the diffusivity, are $L^2 T^{-1}$. Hence show that if the dimensions of Fürtz and Zuber's apparatus for measuring D are reduced to $1/p$ of their original value, the time required for the concentration to reach the value $n = n_1$ at the level $x = l/k$, is reduced to $1/p^2$ of its original value. (l is the total depth of liquid, k is any positive number.) (See Chap. XI, p. 259.)
Also show that if a diffusion experiment of this type performed in a vessel whose dimensions are of the order 5 cm. takes one month, then if the dimensions are reduced to the order one millimetre, the time taken will be of the order 15 minutes.

CHAPTER II

1. Assuming the earth to be a perfectly homogeneous sphere, spinning with angular velocity Ω about its geographic axis, prove that the angle between a straight line drawn from a point P on the earth's surface to the centre and a line drawn from P in the apparent direction of the force of gravity is approximately equal to $\Omega^2 R \sin 2L / 2(g_0 + \Omega^2 R \cos^2 L)$ radians, where L is the latitude of P , R is the radius of the earth, and g_0 is the force on unit mass at P due to attraction only.
2. Assuming that the earth consists of a sphere of radius R and mean density ρ_1 , enclosed in a thin concentric spherical shell of matter of thickness h and mean density ρ_2 , prove that g_1/g_2 , the ratio of the gravitational acceleration at a point on the outer surface to that at a point on the surface of the inner sphere, is $\{1 - 2h/R + 3h\rho_2/R\rho_1\}$ approximately. (Airy's mine experiment.)

3. Show that if a bar pendulum oscillating in air has external symmetry of form about the centre, then $g = 4\pi^2(I_1^2 - I_2^2)/(I_1T_1^2 - I_2T_2^2)$ and du Buat's corrections to T_1^2 and T_2^2 , separately, for extra moment of inertia of carried air are eliminated (Bessel).

4. Referring to p. 20, prove that if the knife-edges are equal cylinders the radius disappears from the expression for T .

5. Referring to p. 20, prove that if the knife-edges are not equal cylinders, then $g(T_1^2 + T_2^2)/8\pi^2 = I_1 + I_2$, where T_1 and T_2 are the measured times of oscillation about the two knife-edges. (Poyse's correction.)

6. Prove that if the support of a bar pendulum yields a distance c to a horizontal force of one dyne, $gT^2/4\pi^2 = I_1 + I_2 + cMg$.

7. Referring to p. 20, prove that if two pendulums, of symmetrical external shape, are of equal weight but have different lengths, and have transferable knife-edges, then

$$g(T_1^2 - T_2^2)/4\pi^2 = I_1 - I_2 \quad (\text{DeJorge's correction})$$

8. Prove equations (30), (40) on p. 34, i.e.

$$R \sin 2\theta = 2U_{xy} \quad \text{and} \quad R \cos \theta = U_{xx}^2 + U_{yy}^2.$$

9. Verify equation (3), p. 14, by direct substitution, i.e. show that

$$\ddot{\theta} = Ae^{-bt} \cos[(c^2 - b^2)t + \phi]$$

is a solution of the equation $\ddot{\theta} + 2b\dot{\theta} + c^2\theta = 0$

10. If g is measured by a pendulum describing oscillations of amplitude 30 mm., show that this necessitates a percentage fractional correction of 9.52×10^{-4} to the result.

11. A simple spiral spring suspended vertically and loaded at the bottom is considered from the point of view of measuring Δg on shifting the position from one station to another. It is proposed to measure the change ΔS in the axial extension. If the minimum sensitivity desirable in such a gravimeter is $\Delta g = 10^{-5}g$, and if the maximum displacement of a spring to be used in a portable

10^{-4}
cm,
koff)

CHAPTER III

1. Defining the normal flux of force through an element dS of a surface drawn in a gravitational field as the product of the normal component $F \cos \theta$ of the force on unit mass and the area dS , prove Gauss's theorem as applied to gravitation, that the total outward normal flux of force over any closed surface is $-4\pi G$ times the mass enclosed.

2. Show that a thin spherical shell of attracting matter of thickness α , mean radius r , and uniform density ρ has the same external field as if all the mass were concentrated in a single particle at its centre. Hence prove that a sphere composed of concentric shells, not necessarily all of the same density, acts in the same way.

3. Apply Gauss's theorem to find the gravitational field (force on unit mass) and potential at points (a) inside the central cavity, (b) inside the material, and (c) outside of a thick spherical shell of matter, of radii r and $r + \alpha$, the density of the matter being ρ .

4. Let the mean density of a non-uniform sphere be ρ_1 , and the density of its uniform crust be ρ_2 . Find the force on unit mass placed at a point h cm. from its surface, inside the crust, the external radius being R cm. ($h \ll R$).

5. Referring to Boys' experiment for measuring G , calculate the value of the angle φ (p. 40) corresponding to the maximum displacing moment, given the values of M , m , l , r and c as on p. 41.

6. Referring to Boys' experiment, calculate the moment of the restoring couple due to the attractions between spheres at different levels, for a given angle $\varphi = 64^\circ 38'$, and prove that it is negligible compared with that due to attractions between spheres at the same level, using the values of M , m , l , r and c on p. 41.

7. Consider two torsion balances of Boys' type, in one of which all the linear dimensions, including those of the large and small spheres, are n times as great as those in the other. Let the material of the spheres be the same in each case, but in the second let the suspension fibre be changed so that the period is the same as that in the first. Prove that the angle of deflection is the same in the two cases. Hence show that with a small balance it is possible to use relatively bigger "large spheres" than are practicable with large balances.

8. (a) What are the dimensions of the quantity A_1 in Hoyt's experiments (p. 43)? (b) What is the effect on the period of oscillation of increasing the linear dimensions of every part of the apparatus to n times their original values?

9. What must be the velocity of a body if its mass when moving is 10 per cent greater than its mass when at rest?

10. Find, to 0.005 per cent, the percentage change in mass of a body whose velocity is one-twentieth of the velocity of light, as compared with its mass at rest.

11. Taking approximate values of the mass of the proton as 2×10^{-24} gm., the elementary protonic charge as 5×10^{-10} e.s.u., and Newton's constant of gravitation G as 7×10^{-8} c.g.s. units, show that the ratio of the electrostatic force of repulsion between two protons to their gravitational force of attraction is about 10^{36} .

CHAPTER IV

1. A uniform beam is clamped at one end and supported on the same horizontal level at the free end. Find the bending moment and the shearing stress at any point and also the maximum depression.

2. A uniform beam is clamped horizontally at one end and has a given concentrated load W and a couple C at the other end. Find the bending moment.

3. A uniform weightless beam clamped horizontally at one end has a concentrated load W at a point d at a distance a from the fixed end. Find the depression at a and at the end of the beam.

4. A light rod is supported symmetrically on two knife-edges a distance $l/2$ apart, where l is the length of the rod. Two weights, each of value W , are suspended from the ends of the rod, and a weight w is attached to its centre. If the centre and the two ends all lie in the same straight line, find the ratio W/w .

5. Find the energy stored in a beam which is clamped at one end and free at the other if the load is w per unit length.

6. Find the energy stored in a light beam as in (4) but with a concentrated load W on the end.

7. Find the energy stored in a stretched wire.

8. Find the energy stored in a stretched flat spiral spring
9. Find the time of angular oscillation of a loaded spring.
10. Show that the depression of (1) a rod with a weight attached to one end, (2) a flat spiral spring, due to the shearing force, is negligible compared with that due to the bending moment and torsion respectively.
11. With a given chemical balance the smallest deflection which can conveniently be measured is 10^{-2} rad., corresponding to a mass of 10^{-6} gm. If the effective length of the balance arm is 50 cm., show that the sensitivity of the chemical balance is less than 10^{-2} of that of a torsion balance whose suspension has a length of 100 cm. and radius of circular cross-section of 10^{-2} cm., made of material whose rigidity modulus is 10^{11} dyne cm. $^{-2}$.
12. A light horizontal cantilever is bent by a concentrated load W applied at a point x so that ψ is the angle of inclination of the tangent at any point x , both x and ψ being measured from the fixed end. Show that if $\psi = 90^\circ$ for $x = a = a_0$, then $g = Wa_0^3/(24Ik^3)$.

CHAPTER V

1. Show that for perfect gases the ratio of the adiabatic to the isothermal elasticity is equal to γ , the ratio of the specific heat at constant pressure to the specific heat at constant volume
2. Deduce equation (17), p. 91.
3. Deduce equation (21), p. 92.

CHAPTER VI

1. Suppose that at time $t = 0$ a seismic wave of the form $\xi = \xi_0 \sin \omega t$ arrives at the vertical pendulum seismograph of pp. 102-105. Assuming that damping is negligible, prove that

$$\theta = \frac{\xi_0 \{\sin \omega t + \frac{A \sin \pi t}{k(\alpha^2 - 1)}\},$$

where $A = -\alpha$, $\alpha = \pi/\omega$, and π has the meaning of the text

2. Draw a graph connecting the angle of lag of the vertical pendulum seismograph of p. 105 behind the seismic wave and α where $\alpha = \pi/\omega$
3. Find the angle of lag in the following special cases.
 - (a) ω great, α very small.
 - (b) $\pi = \omega$, $\alpha = 1$.
 - (c) ω very small, α very great
4. Prove that when the damping coefficient k is great, the sensitiveness of the seismograph is greatest when the natural period of the instrument is great and that of the seismic oscillations is small.

5. With reference to the method of finding the depth of a seismic focus, described on p. 107, prove that if a graph is plotted with new variables $Y = e^{2t^2} - a^2$, $X = 2a^2t$, it will be a straight line. Show how to obtain t_0 and d from such a graph.

6. Show that by simply moving from a point A on the earth's surface to a point B 13 m. vertically above A in "free air" the value of g changes by about 0.01 milligal, or in general $\Delta g = 0.30g \frac{h}{A}$ milligal, where A is the elevation in metres.

CHAPTER VII

1. A spherical soap bubble of radius r deflates itself by expelling the air within it through an orifice of cross-section A sq. cm. Prove that the time taken

for the radius to fall to zero is $\frac{2\sqrt{2\pi}}{7A}\sqrt{\frac{\rho r^2}{T}}$, where ρ is the initial density of the air within, and T is the surface tension of the soap solution.

2. A bubble of gas resting on the surface of a liquid has the form of a segment of a sphere. Its precise form is governed by the law that the potential energy in the surface, due to surface tension, is a minimum, consistent with the condition that the volume of the segment is constant. Prove that the bubble takes a hemispherical form.

3. A small spherical bubble of radius r is accidentally formed at a certain depth below the surface of a liquid. Show that if the bubble contains nothing but the saturated vapour of the liquid it is unstable, that is, it will not return to its initial size, if for any reason it undergoes a slight change of radius. Then find the minimum pressure of the gas which must be present in order that the bubble may be stable. Relate this to "bumping" and "steady boiling".

4. A large drop of mercury rests on a horizontal plate. Light from a horizontal bright filament in a distant lamp falls on the curved side of the drop. The reflected beam enters a horizontal telescope. The vertical height of the latter is adjusted until an image of the filament coincides with the horizontal cross-wire of the telescope. The source is displaced vertically through a distance z and the experiment is repeated. Prove that $z = 2\sqrt{\frac{T}{\rho}}\left(\sin\frac{A'}{2} - \sin\frac{A}{2}\right)$, where T is the surface tension and ρ the density of mercury, and A, A' are the angles made with the vertical by the normal to the surface of the drop at the point of incidence of the light, in the first and second cases. (The incident and reflected beams and the normal are in the same vertical plane.)

5. A cylindrical film of indefinite length, mean radius r_1 , and (small) thickness d , contracts under the influence of surface tension, starting from rest. Prove that the time it takes to contract to a cylinder of mean radius r_2 is

$$t = \sqrt{\frac{\rho d_1 r_1 (r_1 - r_2)}{gT}},$$

where T is the surface tension and ρ is the density.

6. A liquid rises in a tube of any shape under the action of surface tension and reaches equilibrium. Prove that the weight of liquid contained in a cylinder bounded by the free surface of the liquid, by the general level of the liquid outside the tube, and by vertical generators drawn from the curve of contact of liquid and solid down to the general level, is equal to the line integral of the vertical projections of the surface tension acting all round the curve of contact.

7. Using the theorem in Example 6, prove that if two adjacent parallel plates inclined at an angle A to the vertical dip into a liquid, the height through which the liquid rises in the narrow space between the plates is independent of the angle of inclination A .

8. Allowing for the spherical cap, calculate the depression of the mercury inside a circular tube of radius r below the general level outside. Calculate the approximate percentage error in the value of the surface tension obtained by using the elementary formula and taking the depression as that measured to the top (umbilic) of the meniscus, when the tube has a diameter of 1 cm.

9. Obtain the equation of equilibrium of a needle floating on a liquid, regarding the needle as a long cylinder, and assuming an angle of contact equal to zero.

10. Assume that the excess pressure on the inside of any gas balloon is $p = p_0 (1 + \frac{2\sigma}{r})$, where p_0 is the pressure outside the balloon, σ is the surface tension, and r is the radius of the balloon.

11. Show that if two flat plates inclined at a small angle α are placed vertically in a liquid, then the profile curve of the liquid-air interface along either plate is approximately a hyperbola.

CHAPTER IX

1. Determine the root mean square velocity of a hydrogen molecule at N.T.P.; the density of hydrogen at 0° C. is 0.09 grammes/litre.

2. Show that the gas constant R represents two-thirds of the kinetic energy of the molecules of a gramme-molecule of the gas at 1° abs.

3. Prove that γ , the ratio of the specific heats of a gas at constant pressure and constant volume respectively, is given by $\gamma = 1 + \frac{2}{z}$, where z is the number of degrees of freedom of a gas molecule.

4. Prove that the mean velocity \bar{c} and the root mean square velocity C are connected by the relation $\bar{c}/C = (\pi/2)^{1/2}$.

5. Show that $p\bar{v} = 4p(M/2\pi RT)^{1/2}$, where M is the molecular weight of the gas.

6. Show that, owing to the finite molecular diameter σ , the mean free path is reduced from that appertaining to point molecules in the ratio $\lambda_0/\lambda = 1 - 2\sigma/3\lambda$.

7. Deduce Dalton's law of partial pressures, i.e. that the total pressure exerted by a mixture of gases is equal to the sum of the pressures which they would each exert individually if they alone occupied the given volume, on the basis of the kinetic theory of gases.

8. Show that the mean velocity of molecules emitted from a small aperture in the side of an enclosure at temperature T is $C_1 = (4RT/M)^{1/2}$, where M is the molecular weight of the molecules.

9. Prove that the constant b of van der Waals' equation is equal to four times the volume of the molecules.

10. When mercury vapour is pumped away from 2 sq. cm. of surface, the weight of liquid mercury present decreases at the rate of 10^{-4} gm. per sec. Show that if the saturation vapour pressure of mercury at 20° C. is taken as 10^{-4} cm. of mercury, the coefficient of evaporation, which is equal to the accommodation coefficient, is approximately unity.

CHAPTER X

1. Using the symbols on p. 247, prove that for a dilute solution in which a fraction α of the molecules are dissociated, each into v ions,

$$1 - \beta = (v - 1)\alpha n^{-1}/vK$$

2. Referring to pp. 250-1, prove that $1/\epsilon$ is that distance z in which the potential in the neighbourhood of an electrode dipping into a solution containing ions diminishes to $1/e$ of its value at the surface (e being the base of Napierian logarithms).

3. Prove that for an aqueous solution of a single monovalent binary salt at 0°C , $1 - \beta = 0.263(2\gamma)^{\frac{1}{2}}$, where γ is the concentration of the salt in gramme-molecules per litre and D for water is 88.23 c.s.u.

4. Discuss the analogy between the corrections to the perfect gas equation introduced by van der Waals, and those to van't Hoff's equation introduced by Debye and Hückel.

5. Prove that in an aqueous solution of an electrolyte of any type at 0°C , $\alpha = 0.229\Gamma^{\frac{1}{2}}$, where $\Gamma = \sum \gamma_i z_i^2$, z_i is the valency of an ion of type i , and γ_i is the gramme-molecular concentration per litre of those ions.

6. Find the depression of the freezing-point of water by adding KCl to make it into a millinormal solution, and also the osmotic pressure of the solution, assuming complete dissociation of the salt. Which of the two, measurement of freezing-point depression or measurement of osmotic pressure, is likely to be more accurate?

CHAPTER XI

1. Prove that the differential equation representing the diffusion of a salt in solution along a cylinder is $D \frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t}$, it being assumed that there is no lateral escape of the salt.

2. A very tall narrow cylindrical vessel, of length $2L$, is half-filled with a solution of concentration n_0 , and at time $t = 0$ the upper half is filled with pure solvent. Show that the concentration at any height x above the middle, at any subsequent time t , is

$$n = \frac{1}{2}n_0 - \frac{2n_0}{\pi} \left\{ e^{-Dx^2/l^2} \sin \pi x + \frac{1}{2}e^{-4Dx^2/l^2} \sin 2\pi x + \dots \right\},$$

where $x = \pi/2L$, and D , the diffusivity, is independent of the concentration.

3. Show that in Färth and Zuber's experiment, Case I, when $x \ll l$, the concentration in the lower part of the liquid, where $0 > x > -\infty$, can be expressed as

$$n = \frac{1}{2}n_0 \left\{ 1 + \frac{2}{\pi^{\frac{1}{2}}} \int_0^y e^{-y^2} dy \right\},$$

where $y^2 = x^2/(4Dt)$.

4. Assuming that the initial condition in the lower half is that $n = n_0$ everywhere when $t = 0$, show that if n is $x \ll l$,

$$n = \frac{1}{2}n_0 \left\{ 1 - \frac{2}{\pi^{\frac{1}{2}}} \int_0^y e^{-y^2} dy \right\},$$

where $y^2 = x^2/(4Dt)$.

5. Show that if the diffusion rate in a crystalline solid is doubled when the absolute temperature T is doubled, then the activation energy E for the transfer of an atom from one adjacent position in the lattice to another is about $3.4 kT$.

CHAPTER XII

1. The end of a capillary tube, whose bore is a circular cylinder of radius r cm., is dipped in a liquid, the axis of the cylinder making an angle θ with the vertical. The viscosity of the liquid is η . The tube is open at both ends and

the bore is moistened beforehand with the liquid. The liquid rises in the tube. Prove that the velocity with which the liquid ascends the tube is $\frac{p^2 \cos \theta (l^2 x - l)}{8\eta}$

at any instant, where p is the density of the liquid, x is the instantaneous length of the column of liquid, and l is the final length when equilibrium is reached.

2. Two flat circular discs of radius a are mounted coaxially, parallel to one another at a distance d apart, and the lower one is rotated with constant angular velocity ω . Neglecting edge corrections, find the torque communicated to the upper disc if η is the coefficient of viscosity of the medium surrounding the discs.

3. Show from simple energy considerations that for turbulent flow as in a rotameter, the rate of discharge Q is proportional to the square root of the pressure difference p .

4. A very viscous liquid is forced into a capillary tube of radius r at high pressure P . Assuming streamline flow, show that if t is the time taken for the fluid to change in length in the capillary by $(l - l_0)$, then $\eta = Pr^3 t / 4(P - l_0^2)$.

CHAPTER XIII

1. In a certain experiment the following values of the mechanical equivalent of heat were obtained: 4.169×10^7 , 4.150×10^7 , 4.181×10^7 , 4.151×10^7 , 4.180×10^7 , and 4.175×10^7 ergs per calorie. Calculate the arithmetic mean and its probable error.

2. Sherratt and Awbery obtained the following values of the velocity of sound in the air in a certain tube: 327.7, 327.1, 327.9, 327.3, 327.9, 327.6 and 327.6 metres per second. Calculate the arithmetic mean and the probable error.

3. C. V. Boys made nine observations on the mean density ρ of the earth. Four of them were made under favourable conditions, giving $\rho = 5.5291$, 5.5285, 5.5306 and 5.5309 grammes per c.c. respectively. The other five results, made under less favourable conditions, were $\rho = 5.5213$, 5.5151, 5.5159, 5.5189 and 5.5172 grammes per c.c. respectively. Calculate the arithmetic mean and its probable error, using (a) the first four results and (b) all nine results. (Boys gave $\rho = 5.527$ as the best value to be derived from his experiments and did not calculate a probable error. See his comments in *Dictionary of Applied Physics*, Vol. III, p. 262.)

4. Six different methods give the following values of Planck's constant: $(6.547 \pm 0.011) \times 10^{-27}$, $(6.580 \pm 0.015) \times 10^{-27}$, $(6.550 \pm 0.000) \times 10^{-27}$, $(6.545 \pm 0.010) \times 10^{-27}$, $(6.545 \pm 0.015) \times 10^{-27}$ and $(6.539 \pm 0.010) \times 10^{-27}$ erg sec. Calculate the weighted mean of these results and its probable error.

5. A right circular cylinder has a length l cm., which is measurable with a probable error of $\pm x_l$, and a radius r cm., which is measurable with a probable error of $\pm x_r$. What is the area of its curved surface and what is the probable error of that value?

6. On the flat face of a hemisphere of radius $r \pm x_r$ there stands a right circular cone whose base has the same radius $r \pm x_r$ and whose height is $h \pm x_h$. Find the volume of the whole body and its probable error.

7. Ferguson and Miller measured the specific heat of benzene at various temperatures. In one set of experiments their results were: $S = 0.3993$ at 22.61°C ; $S = 0.4025$ at 23.62°C ; $S = 0.4002$ at 30.59°C ; $S = 0.4220$ at 39.51°C ; $S = 0.4264$ at 43.53°C ; $S = 0.4321$ at 44.36°C . Assuming that $S = a + b/(t - 20)$, where t is the temperature, calculate a and b by the method of least squares.

ANSWERS AND HINTS FOR SOLUTION

CHAP. I.

1. Take surface tension, density, and radius of drop as variables: $t \propto \rho^{1/2} \gamma^{2/3} S^{-1/2}$.
2. Take coefficient of viscosity, radius of tube, and pressure gradient down tube as variables: $V = \pi p r^4 / 8 l \eta$.
3. $F = 6\pi\eta va$.
4. Take O , K , d , c , v , and v as variables.
5. $R = \frac{1}{2} g^2 a^2 / c^2$.

CHAP. II.

1. Calculate the force due to motion of P round a circle of latitude. Find the sine of the angle required, neglect small terms, and use the binomial theorem.
2. Express g_1 as the sum of the attractions of the inner sphere and of the shell, using the law of gravitation. Use the binomial theorem to obtain approximations.
10. Use equation (9) of section 3.
11. Use $\Delta S = S \cdot \Delta g / g$. $\Delta S = 2 \times 10^{-8}$ cm. This is much less than the limits quoted for the two instruments.

CHAP. III.

1. Consider the flux through dS due to a single particle. Introduce the solid angle subtended by dS .
2. Apply Gauss's theorem.
3. (a) Zero. (b) $4\pi G\rho\{R^3 - r^3\}/3R^2$. (c) $4\pi G\rho\{(r+a)^3 - r^3\}/3R^2$.
4. $4\pi GR\{\rho_1 + (2\rho_1 - 3\rho_2)h/R + 3(\rho_1 - \rho_2)h^2/R^2\}/3$.
5. $64^\circ 38'$.
6. Moment of couple is $2GM \sin \varphi / \{k^2 + l^2 + r^2 + 2lr \cos \varphi\}^{3/2}$, where h is the difference in level.
7. Obtain an expression for θ from the various equations on pp. 40, 41. Write nl for l , &c.
8. (a) +2 of mass, -1 of length, 0 of time. (b) No effect.
9. $c/3.316$.
10. 0.125 per cent.
11. $F_G = GM^2/d^2$; $F_E = Q^2/d^2$.

CHAP. IV.

1. End conditions are
- $y = Dy = 0$
- for
- $x = 0$
- ,
- $y = D^3y = 0$
- for
- $x = l$
- .

$$G = u(\frac{1}{2}x^2 - \frac{1}{2}lx + \frac{1}{6}l^2), \quad F = u(\frac{1}{2}l - x)$$

Maximum depression when $Dy = 0$, given by $x(\frac{1}{2}x^2 - \frac{1}{2}lx + \frac{1}{6}l^2) = 0$

- 2.
- $qAk^2D^2y = G = (G + Wl) - Wx$
- at any point
- x
- . Also when
- $x = 0$
- ,
- $y = Dy = 0$
- ; If
- $\theta_1 =$
- slope at
- $x = l$
- ,
- $qAk^2 \tan \theta_1 = (G + Wl) - \frac{1}{2}Wl$
- , and
- θ_1
- may be written approximately for
- $\tan \theta_1$
- .

$$G = \frac{qAk^2}{l^2} \{y_1(6l - 12x) - l\theta_1(2l - 3x)\}.$$

- 3.
- $qAk^2D^2y = W(a - x)$
- .

If $y_1 =$ depression at A and $y_2 =$ depression at end of beam,

$$qAk^2y_1 = \frac{1}{2}Wa^2, \quad qAk^2y_2 = Wa^2(l/2 - a/6).$$

4. Let the reaction at each of the knife edges be
- R
- . Consider separately (1) the portion of the rod between the mid-point and a knife-edge, (2) the portion between a knife-edge and the nearest end of the rod.

For (1), equation (12) becomes

$$qAk^2D^2y = R(l/4 - x) - W(l/2 - x),$$

where x is measured from the centre of the rod

For (2), equation (12) becomes

$$qAk^2D^2y = Wx,$$

where x is measured from the end of the rodFor the two sections, the boundary conditions at the knife-edge must give the same slope Dy .Answer, $W/w = 5/22$.

5. Bending moment at distance
- x
- from free end is
- $G = \frac{1}{2}wx^2$
- . Hence from (23)

$$V = \int_0^x \frac{w^2x^2}{8qAk^2} dx = \frac{w^3x^3}{40qAk^2}$$

- 6.
- $V = \frac{1}{2} \frac{W^2l^3}{qAk^2}$
- ,
- $y_1 = \frac{1}{2} \frac{Wl^3}{qAk^2}$
- , and hence
- $V = \frac{1}{2}Wy_1$
- .

- 7.
- $\frac{1}{2}Wx$

- 8.
- $\frac{1}{2}Wx = \frac{W^2L^2}{\pi aE^2} = \frac{1}{2}\pi a^2R^2\phi^2$
- .

9. If the tangent to the lower end of the spiral is twisted through an angle
- ϕ
- , the bend per unit length is
- ϕ/l
- . To produce this bend, a couple
- $C = \phi/l \cdot qAl^2$
- must be applied. Hence if
- I_b
- and
- I_s
- are the moments of inertia of bar and spring respectively,

$$(I_b + I_s) \frac{d^2\phi}{dx^2} = -\frac{\phi}{l} qAl^2,$$

which is of the form

$$\frac{d^2\phi}{dx^2} = -m^2\phi, \quad \text{where } m^2 = \frac{qAl^2}{(I_b + I_s)l}$$

Hence

$$\phi = 2\pi \sqrt{\frac{I_b + I_s}{qAl^2l}} = 2\pi \sqrt{\frac{I_b + \frac{1}{4}\pi a^4}{q\pi R^2/l}}$$

10. (a) Rod. From Ex. 3, depression due to bending $= y_1 = \frac{1}{3} \frac{gAk^2}{W^2}$. Depression due to shearing stress $= y_2 = \frac{W}{A} \cdot \frac{l}{\pi}$. Hence $\frac{y_2}{y_1} = \frac{3g}{\pi} \left(\frac{l}{l}\right)^2$; for a square section, side b , $k^2 = b^2/12$.

Hence $\frac{y_2}{y_1} = \frac{g}{4\pi} \left(\frac{l}{l}\right)^2$, and since $b \ll l$, $y_2 \ll y_1$.

(b) Spring. Depression x_1 due to torsion $= 2Wl^2/\pi\mu R^4$; depression x_2 due to shear $= Wl/\pi\mu R^2$.

Hence $x_2/x_1 = \frac{1}{2}(R/a)^2$, and since $R \ll a$, $x_2 \ll x_1$.

11. For torsion balance, angular deflection $\phi = 2Ql/\pi ar^2 = 2 \times 10^{-5} \times g \times 50 \times 10^3/\pi \times 10^{12} \times 10^{-12} = 10^{-3}g/\pi \simeq 100/\pi$ compared with $0 \sim 10^{-3}$ for chemical balance; hence $\theta/\phi < 10^{-3}$.

12. Analysis is formally similar to that for the rise of liquid along a vertical flat plate under surface tension forces (see Chapter VII, § 3) since for the cantilever the couple is a first-order function of x which is proportional to the curvature at the point, whereas for the liquid the pressure, which is a first-order function of y , is likewise proportional to the curvature. For the cantilever

$$G = W(\pi - x) = gAk^2 d\psi/ds = gAk^2 \cos \psi d\psi/dx.$$

Hence $Wa^3 = 2gAk^2 \sin \psi$ which for $\psi = 90^\circ$ gives $g = Wa^3/2Ak^2$.

CHAP. V.

1. Use the equations $pv = k$, $p\nu = k$ to deduce the two compressibilities.

CHAP. VI.

3. (a) $\delta = \pi$; (b) $\delta = \pi/2$; (c) $\delta = 0$.

CHAP. VII.

1. Introduce a symbol for the velocity of efflux. Assume that the loss of potential energy during an elementary contraction is equal to the gain of kinetic energy of efflux in the same time. Eliminate the velocity of efflux between two equations.

2. The flat face of the segment does not enter into the expression for the surface energy. Find the conditions for a minimum surface tension and constant volume by elementary calculus methods.

3. Write down the equation of equilibrium of the bubble as far as pressures are concerned, and consider the effect of a slight change of radius.

4. Begin with the equation of the meridional profile curve of a large drop.

5. The total mass of the annular cylinder remains constant. The loss of potential energy of the film is equal to its gain of kinetic energy. Introduce a symbol for the radial velocity.

6. Write down the weight of an elementary cylinder of height dz and upper surface dS . Use the differential equation of the free surface (equation (4), p. 119) to change the form of the expression, and integrate. Introduce an expression for the difference $dS' - dS$, where dS' is an element of a surface S' , obtained from S by marking off points along normals to S , at a constant distance dn from S . Use this expression to change the form of the expression for the weight of the cylinder.

7. Write down expressions for the two quantities mentioned in Ex. 6 and equate them. The angle of contact is not equal to zero. Use the height measured in the centre of the narrow space.

8. Use Archimedes' theorem to find the area of the curved surface of the cap and hence its volume.

9. Assume contact all round the lower part of the cylinder. Apply the equation of the profile curve of a right section of the system (see p. 120). Include a term for the upthrust on the immersed parts.

10. Draw a central section through the axis of revolution, and consider what are the principal radii of curvature. Find one of them from the figure and use equation (4), p. 119, to find the other. Note that in a rubber or other membrane the tension is not the same in all directions.

11. An elementary vertical slice of liquid, bounded by the two plates and two parallel vertical planes distant x and $x + \delta x$ from the thin edge of the wedge, is at rest because its weight is balanced by an equal resultant upward force due to surface tension γ (see on the free surface above). If the two meniscuses of the

CHAP. IX.

1. 1700 metres/sec.

4. Use Maxwell's law of distribution of velocities.

5. If α represents the most probable velocity of the gas molecules, Maxwell's distribution law may be written

$$N_{dc} = \frac{4N}{\pi^{\frac{3}{2}}} c^2 e^{-\frac{1}{2}\alpha^2 c^2} dc,$$

where N_{dc} is the fraction of the N molecules present whose velocity lies between c and $c + dc$, and k is Boltzmann's constant. The mean square velocity of the molecules issuing from a small aperture in a uniform temperature enclosure will be

$$C_1^2 = \frac{\int_0^\infty \frac{4N}{\pi^{\frac{3}{2}}} c^2 e^{-\frac{1}{2}\alpha^2 c^2} c^2 dc}{\int_0^\infty \frac{4N}{\pi^{\frac{3}{2}}} c^2 e^{-\frac{1}{2}\alpha^2 c^2} dc} = 2\alpha^2,$$

since $C_1^2 = \frac{\sum N_{dc} c^2}{\sum N_{dc}}$, where N_{dc} is the number of molecules emerging with velocity c . Inside the enclosure $C^2 = 3\alpha^2/2$; hence $C_1^2 = \frac{4}{3} C^2 = 4kT/m$.

6. The average distance of approach of two molecules is

$$\bar{r} = \int_0^{\pi/2} \frac{2\pi v \sigma^2 \sin^2 \theta \cos \theta}{\pi \sigma^2 v} d\theta = \frac{2}{3}\sigma$$

8. The product of c^2 and the number of molecules in the emitted beam, that is, cN_{dc} , must be integrated from zero to infinity and divided by the integral of the number of particles issuing with velocity c ; hence

$$C_1^2 = \frac{\int_0^\infty \frac{4N}{\pi^2 c^2} c^2 \times c \times c^2 e^{-c^2/c^2} dc}{\int_0^\infty \frac{4N}{\pi^2 c^2} c \times c^2 e^{-c^2/c^2} dc}.$$

9. The average distance of approach of two spherical molecules is $2\sigma/3$, by Ex. 6, where σ is the diameter of the molecules. Hence the mean free path is shortened, compared with its value for disc-like molecules, by the amount $\lambda_2 = \lambda - 2\sigma/3$. Hence, using this expression and equation (2), p. 134, we have

$$\frac{\lambda_2}{\lambda} = 1 - \frac{2\sigma/3}{\lambda} = 1 - \frac{2}{3} \frac{\pi \sigma^2 n}{V} = \frac{V - 4(\frac{1}{2} \pi \sigma^2 n)}{V}.$$

10. Loss in weight in gm. per sq. cm. per sec. is $\alpha p/(2\pi RT)^{\frac{1}{2}}$, where α is the coefficient of evaporation and R is the gas constant per gramme.

CHAP. X.

1. Apply the law of mass action to prove that $\alpha^n n^{n-1} = K(1 - \alpha)$; then prove that $P = k_B \{n(1 - \alpha) + \alpha n\}$, from van't Hoff's law, and evaluate $1 - \beta = (P_s - P)/P_s$.

6. Depression of freezing-point = 0.00368°C . Osmotic pressure = 36 mm. Hg. The latter can be measured more accurately.

CHAP. XI.

2. As in problems on conduction of heat along a bar, consider the solute entering and leaving a slice of thickness dx . Hence deduce $\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$. The solution $n = Ae^{-2\sigma^2 t} \sin \alpha x$ is appropriate here. Apply the boundary and initial conditions and use Fourier's theorem. Note that at the top of the tube $\frac{\partial n}{\partial x} = 0$, for all values of t .

5. $D_1/D_2 = \exp(-E/kT)/\exp(-L/2kT)$.

CHAP. XII.

1. Write down Poiseuille's equation as applied to the column at any instant, and also an expression for the pressure difference on the two sides of the hemispherical meniscus. The lower end of the tube only just enters the liquid.

2. Find the elementary torque acting on an annulus of radii r and $r + dr$. The total torque $\Gamma \propto \pi \eta \omega a^4/2d$.

3. Rate of supply of energy is pQ , which equals kinetic energy imparted $\frac{1}{2} Q \rho v^2$; also $Q = vA$ where A is area of cross-section.

4. Rate of flow $Q/t = \pi r^2(l - l_0)$; average pressure gradient is $2P/(l_1 + l_0)$.

CHAP. XIII.

1. $(4.178 \pm 0.001) \times 10^3$ ergs per calorie.2. 537.69 ± 0.07 metres per second.3. (a) 5.5283 ± 0.0005 grammes per c.c.(b) 5.5225 ± 0.0012 grammes per c.c.4. $(6.5468 \pm 0.0017) \times 10^{-22}$ erg sec.5. Area = $2\pi r^2$ sq. cm.Probable error $\alpha = 2\pi(r^2\alpha_1^2 + r^4\alpha_2^2)^{1/2}$.6. Volume = $\frac{\pi}{3}(2r^3 + hr^3)$.Probable error $\alpha = \left\{ \left(2\pi r^2 + \frac{2h\pi r}{3} \right)^2 \alpha_1^2 + \left(\frac{\pi r^2}{3} \right)^2 \alpha_2^2 \right\}^{1/2}$.7. $S = 0.3956 + 0.001287(t - 20)$.

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